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70682

## SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: V. Monchalan Examiner #: 62637 Date: 9/30/02  
 Art Unit: 1764 Phone Number 308-384-4 Serial Number: 09/016509  
 Mail Box and Bldg/Room Location: 103 16 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

\*\*\*\*\*  
 Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of Invention: Difluoromethane Purification Method  
 Inventors (please provide full names): Paul G. Clemmer

Earliest Priority Filing Date: 25 June 2001

\*For Sequence Searches Only\* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

*Pls. provide detailed claims 184-7*

*Thanks*

## STAFF USE ONLY

	Type of Search	Vendors and cost where applicable
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FILE 'REGISTRY' ENTERED AT 12:05:47 ON 01 OCT 2002  
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FILE 'REGISTRY' ENTERED AT 11:34:48 ON 01 OCT 2002  
E DIFLUOROMETHANE/CN  
L1 1 SEA DIFLUOROMETHANE/CN  
E DICHLOROMETHANE/CN  
L2 1 SEA DICHLOROMETHANE/CN

FILE 'HCA' ENTERED AT 11:38:57 ON 01 OCT 2002  
L3 2957 SEA L1 OR DIFLUOROMETHANE# OR METHYLENE#(A) (FLUORIDE# OR  
DIFLUORIDE#) OR CH2F2 OR CF2H2 OR H2CF2 OR F2CH2 OR  
H2F2C OR F2H2C  
L4 96388 SEA L2 OR DICHLOROMETHANE# OR METHYLENE#(A) (CHLORIDE# OR  
DICHLORIDE#) OR CH2CL2 OR CCL2H2 OR H2CCL2 OR CL2CH2 OR  
H2CL2C OR CL2H2C  
L5 347818 SEA DISTILL? OR DIST# OR DISTN# OR CODISTILL? OR CODIST#  
OR CODISTN# OR AZEOTROP? OR COAZEOTROP?  
L6 916098 SEA EXTRACT? OR EXT# OR EXTN#  
L7 29 SEA L3 AND L4 AND L5  
L8 1 SEA L7 AND L6

FILE 'REGISTRY' ENTERED AT 11:45:42 ON 01 OCT 2002  
L9 63298 SEA C CL/ELF OR C CL F/ELF OR C H CL/ELF OR C H F CL/ELF  
L10 256 SEA L9 AND 1/C AND 1/NC  
L11 255 SEA L10 NOT (L1 OR L2)

FILE 'HCA' ENTERED AT 11:54:49 ON 01 OCT 2002  
L12 67450 SEA L11  
L13 9 SEA L7 AND L12  
L14 9 SEA L13 NOT L8  
L15 19 SEA L7 NOT (L8 OR L14)

FILE 'WPIDS' ENTERED AT 11:57:07 ON 01 OCT 2002  
L16 727 SEA L1 OR DIFLUOROMETHANE# OR METHYLENE#(A) (FLUORIDE# OR  
DIFLUORIDE#) OR CH2F2 OR CF2H2 OR H2CF2 OR F2CH2 OR  
H2F2C OR F2H2C  
L17 15238 SEA L2 OR DICHLOROMETHANE# OR METHYLENE#(A) (CHLORIDE# OR  
DICHLORIDE#) OR CH2CL2 OR CCL2H2 OR H2CCL2 OR CL2CH2 OR  
H2CL2C OR CL2H2C  
L18 78875 SEA DISTILL? OR DIST# OR DISTN# OR CODISTILL? OR CODIST#  
OR CODISTN# OR AZEOTROP? OR COAZEOTROP?  
L19 19 SEA L16 AND L17 AND L18  
L20 266343 SEA EXTRACT? OR EXT# OR EXTN#  
L21 4 SEA L19 AND L20  
L22 15 SEA L19 NOT L21

FILE 'REGISTRY' ENTERED AT 12:05:47 ON 01 OCT 2002

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FILE 'HCA' ENTERED AT 12:05:59 ON 01 OCT 2002

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L8 ANSWER 1 OF 1 HCA COPYRIGHT 2002 ACS

130:169822 Purification of **difluoromethane** by

**extractive distillation.** Boehmer, Sara W.;

Mahler, Barry Asher; Miller, Ralph Newton (E.I. Du Pont De Nemours

and Company, USA). PCT Int. Appl. WO 9907660 A1 19990218, 30 pp.

DESIGNATED STATES: W: JP, US; RW: AT, BE, CH, CY, DE, DK, ES, FI,  
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. (English). CODEN: PIXXD2.

APPLICATION: WO 1998-US16689 19980812. PRIORITY: US 1997-55502  
19970812.

AB The facile and economically attractive **extractive**

**distn.** of **difluoromethane** from mixts. comprising

it and .gtoreq.1 of chlorodifluoromethane, 1,1,1-trifluoroethane,

chloropentafluoroethane, and pentafluoroethane using hydrocarbon

(e.g., n-pentane), chlorocarbon (**dichloromethane**), and  
oxygen-contg. (e.g., EtOH) **extractive** agents is described.

A process flow diagram is presented.

IT 75-09-2, **Dichloromethane**, uses

(**extractive distn.** agents; purifn. of

**difluoromethane** by **extractive distn.**)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5P, **Difluoromethane**

(purifn. of **difluoromethane** by **extractive**

**distn.**)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IC ICM C07C017-386

ICS C07C019-08

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 23, 48

ST **difluoromethane extractive distn**

- IT Alkanes, uses  
Hydrocarbons, uses  
(chloro, **extractive distn.** agents; purifn. of  
difluoromethane by **extractive distn.**)
- IT Alcohols, uses  
Alkanes, uses  
Cycloalkanes  
Ketones, uses  
(**extractive distn.** agents; purifn. of  
difluoromethane by **extractive distn.**)
- IT Distillation  
(**extractive**; purifn. of difluoromethane by)
- IT 64-17-5, Ethanol, uses 67-56-1, Methanol, uses 67-63-0,  
2-Propanol, uses 67-64-1, Acetone, uses 71-23-8, 1-Propanol,  
uses 75-09-2, Dichloromethane, uses 78-93-3,  
Butanone, uses 96-14-0, 3-Methylpentane 96-37-7,  
Methylcyclopentane 107-83-5, 2-Methylpentane 109-66-0,  
n-Pentane, uses 110-54-3, n-Hexane, uses 110-82-7, Cyclohexane,  
uses 142-82-5, n-Heptane, uses 287-92-3, Cyclopentane  
(**extractive distn.** agents; purifn. of  
difluoromethane by **extractive distn.**)
- IT 75-10-5P, Difluoromethane  
(purifn. of difluoromethane by **extractive  
distn.**)
- IT 75-45-6, Chlorodifluoromethane 76-15-3 354-33-6,  
Pentafluoroethane 420-46-2, 1,1,1-Trifluoroethane  
(purifn. of difluoromethane by **extractive  
distn.** from mixts. contg.)

=> d l14 1-9 cbib abs hitstr hitind

- L14 ANSWER 1 OF 9 HCA COPYRIGHT 2002 ACS
- 132:280892 Method of producing hydrofluorocarbons. Logsdon, Peter B.  
(Alliedsignal Inc., USA). PCT Int. Appl. WO 2000024696 A1 20000504,  
26 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA, BB, BG, BR,  
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID,  
IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD,  
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,  
TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU,  
TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI,  
FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG.  
(English). CODEN: PIXXD2. APPLICATION: WO 1999-US25202 19991028.  
PRIORITY: US 1998-181174 19981028.
- AB A process for producing fluorinated org. compds. comprising reacting  
an org. compd. (e.g., CH<sub>2</sub>Cl<sub>2</sub>) and fluorination agent  
(e.g., HF) in the presence of a fluorination catalyst, while  
maintaining a pressure less-than-sufficient for high-temp.  
**distn.**, to produce the desired fluorinated carbon compd.  
(e.g., CH<sub>2</sub>F<sub>2</sub>).
- IT 74-87-3P, HCC-40, preparation  
(method of producing hydrofluorocarbons)

RN 74-87-3 HCA  
 CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)

$\text{H}_3\text{C}-\text{Cl}$

IT 75-71-8P, CFC-12  
 (method of producing hydrofluorocarbons)  
 RN 75-71-8 HCA  
 CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



IT 75-10-5P, Difluoromethane  
 (method of producing hydrofluorocarbons)  
 RN 75-10-5 HCA  
 CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

$\text{F}-\text{CH}_2-\text{F}$

IT 75-09-2, Dichloromethane, reactions  
 (method of producing hydrofluorocarbons from)  
 RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

$\text{Cl}-\text{CH}_2-\text{Cl}$

IC ICM C07C017-20  
 ICS C07C017-383; C07C019-08  
 CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 23, 48  
 ST difluoromethane, manuf dichloromethane  
 fluorination; distn purifn difluoromethane;  
 fluorocarbon manuf  
 IT Distillation  
 (low-temp.; method of producing purified hydrofluorocarbons  
 using)  
 IT 74-87-3P, HCC-40, preparation 75-43-4P, HCFC-21  
 75-45-6P, HCFC-22 75-46-7P, HFC-23  
 (method of producing hydrofluorocarbons)  
 IT 75-71-8P, CFC-12  
 (method of producing hydrofluorocarbons)  
 IT 75-10-5P, Difluoromethane  
 (method of producing hydrofluorocarbons)  
 IT 75-09-2, Dichloromethane, reactions 7664-39-3,

Hydrogen fluoride, reactions  
(method of producing hydrofluorocarbons from)

L14 ANSWER 2 OF 9 HCA COPYRIGHT 2002 ACS

130:353931 Method of producing hydrofluorocarbons by the catalytic fluorination of chlorocarbons with hydrogen fluoride at reduced pressure with reduced use of catalyst oxidizing reactivators as well as reduced catalyst deactivation and reduced byproduct formation. Bass, John Stephen; Scheidle, Peter Heinz (AlliedSignal Inc., USA). PCT Int. Appl. WO 9926906 A2 19990603, 17 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1998-US25032 19981123. PRIORITY: US 1997-975311 19971121.

AB A method of producing hydrofluorocarbons (e.g., difluoromethane) is achieved by the catalytic fluorination of chlorocarbons (e.g., dichloromethane) with hydrogen fluoride at reduced pressures with subsequent reduced catalyst deactivation and thus a reduced use of catalyst oxidizing reactivator as well as reduced byproduct (e.g., chlorofluoromethane) formation.

IT 74-87-3P, HCC 40, preparation  
(method of producing hydrofluorocarbons by the catalytic fluorination of chlorocarbons with hydrogen fluoride at reduced pressures with reduced catalyst deactivation and byproduct formation)

RN 74-87-3 HCA

CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)

H<sub>3</sub>C-Cl

IT 75-10-5P, Difluoromethane

(method of producing hydrofluorocarbons by the catalytic fluorination of chlorocarbons with hydrogen fluoride at reduced pressures with reduced catalyst deactivation and byproduct formation)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IT 75-09-2, Methylene chloride, reactions

(method of producing hydrofluorocarbons by the catalytic fluorination of chlorocarbons with hydrogen fluoride at reduced pressures with reduced catalyst deactivation and byproduct formation)

RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

- IC ICM C07C017-00  
CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48  
ST **difluoromethane** manuf fluorination **dichloromethane**  
; hydrofluorocarbon manuf low pressure fluorination  
hydrochlorocarbon; catalyst deactivation redn hydrofluorocarbon  
manuf  
IT **Distillation**  
(low-temp., purifn. step; method of producing hydrofluorocarbons  
by the catalytic fluorination of chlorocarbons with hydrogen  
fluoride at reduced pressures with reduced catalyst deactivation  
and byproduct formation)  
IT 74-87-3P, HCC 40, preparation 75-43-4P, HCFC 21  
(method of producing hydrofluorocarbons by the catalytic  
fluorination of chlorocarbons with hydrogen fluoride at reduced  
pressures with reduced catalyst deactivation and byproduct  
formation)  
IT 75-10-5P, **Difluoromethane**  
(method of producing hydrofluorocarbons by the catalytic  
fluorination of chlorocarbons with hydrogen fluoride at reduced  
pressures with reduced catalyst deactivation and byproduct  
formation)  
IT 75-09-2, **Methylene chloride**, reactions  
7664-39-3, Hydrogen fluoride, reactions  
(method of producing hydrofluorocarbons by the catalytic  
fluorination of chlorocarbons with hydrogen fluoride at reduced  
pressures with reduced catalyst deactivation and byproduct  
formation)  
L14 ANSWER 3 OF 9 HCA COPYRIGHT 2002 ACS  
128:192355 Process for producing **difluoromethane**. Tsuda,  
Takehide; Shibamura, Takashi (Daikin Industries Ltd., Japan; Tsuda,  
Takehide; Shibamura, Takashi). PCT Int. Appl. WO 9808790 A1  
19980305, 18 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA, BB,  
BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU,  
IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK,  
MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, UA, UG, US, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ,  
TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FI, FR, GA,  
GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG.  
(Japanese). CODEN: PIXXD2. APPLICATION: WO 1997-JP2963 19970826.  
PRIORITY: JP 1996-224846 19960827.  
AB Characterized is a process for refining **difluoromethane** by  
removing water which is contained in **difluoromethane**.  
This process comprises **distg. difluoromethan**  
contg. water to recover a **distillate** comprising

difluoromethane and bottoms comprising a mixt. of water-contg. difluoromethane with chlorofluoromethane and/or dichloromethane. The bottoms are recycled to the reaction steps to be reused together with the feedstock.

IT 75-09-2P, Dichloromethane, preparation  
75-10-5P, HFC-32 75-69-4P, CFC-11 75-71-8P  
, CFC-12 75-72-9P, CFC-13  
(process for producing difluoromethane)  
RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

RN 75-69-4 HCA  
CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-71-8 HCA  
CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-72-9 HCA  
CN Methane, chlorotrifluoro- (8CI, 9CI) (CA INDEX NAME)



IC ICM C07C019-08  
ICS C07C017-20; C07C017-383; B01J027-10



- CC 23-3 (Aliphatic Compounds)  
 ST **difluoromethane** purifn **distn**  
 IT **Distillation**  
 (process for producing **difluoromethane** by **distn**)
- IT 75-09-2P, **Dichloromethane**, preparation  
 75-10-5P, HFC-32 75-69-4P, CFC-11 75-71-8P  
 , CFC-12 75-72-9P, CFC-13 76-13-1P, CFC-113 593-70-4P,  
 HCFC-31  
 (process for producing **difluoromethane**)
- L14 ANSWER 4 OF 9 HCA COPYRIGHT 2002 ACS  
 128:36364 **Azeotropic distillation** process for  
 separating **difluoromethane** from dichlorofluoromethane.  
 Cerri, Gustavo; Kong, Kin Ching; Swain, Charles Frances; Basu, Rajat  
 Subhra (AlliedSignal Inc., USA). PCT Int. Appl. WO 9744301 A1  
 19971127, 14 pp. DESIGNATED STATES: W: JP, KR; RW: AT, BE, CH, DE,  
 DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. (English).  
 CODEN: PIXXD2. APPLICATION: WO 1997-US8674 19970522. PRIORITY: US  
 1996-652891 19960523.
- AB Dichlorodifluoromethane is sepd. from **difluoromethane** by  
 making use of the **azeotrope** formed by these 2 compds. and  
 removing the **difluoromethane** as a **distn.** bottoms  
 product.
- IT 75-71-8P, Dichlorodifluoromethane  
 (**azeotropic distn.** process for sepg.  
 dichlorodifluoromethane from **difluoromethane**)
- RN 75-71-8 HCA  
 CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



- IT 75-10-5, **Difluoromethane**  
 (**azeotropic distn.** process for sepg.  
 dichlorodifluoromethane from **difluoromethane**)
- RN 75-10-5 HCA  
 CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)



- IT 75-09-2, **Dichloromethane**, reactions  
 (**azeotropic distn.** process for sepg.  
 dichlorodifluoromethane from **difluoromethane**)
- RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

- IC ICM C07C017-383  
ICS C07C019-10; C07C017-20; C07C017-23
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48
- ST chlorofluoromethane purifn **azeotropic distn**;  
fluoromethane removal chlorofluoromethane **azeotropic distn**
- IT **Distillation**  
(**azeotropic**; for sepg. dichlorodifluoromethane from difluoromethane)
- IT Purification  
(of dichlorodifluoromethane from difluoromethane by **azeotropic distn.**)
- IT 75-71-8P, Dichlorodifluoromethane  
(**azeotropic distn.** process for sepg. dichlorodifluoromethane from difluoromethane)
- IT 75-10-5, Difluoromethane  
(**azeotropic distn.** process for sepg. dichlorodifluoromethane from difluoromethane)
- IT 75-09-2, Dichloromethane, reactions 593-70-4,  
Chlorofluoromethane 7664-39-3, Hydrogen fluoride, reactions  
(**azeotropic distn.** process for sepg. dichlorodifluoromethane from difluoromethane)
- L14 ANSWER 5 OF 9 HCA COPYRIGHT 2002 ACS
- 126:80290 A relationship between dynamic viscosity and reduced temperature of refrigerant fluids and their mixtures in the liquid phase. Latini, Giovanni; Passerini, Giorgio; Polonara, Fabio (Dipartimento di Energetica, Universita di Ancona, Via Brecce Bianche, I-60100, Ancona, Italy). Fluid Phase Equilibria, 125(1-2, 4th Asian Thermophysical Properties Conference, 1995), 205-217 (English) 1996. CODEN: FPEQDT. ISSN: 0378-3812. Publisher: Elsevier.
- AB A prediction method relating dynamic viscosity with reduced temp. is proposed in this paper for pure and mixed refrigerant fluids in the liq. state along the satn. line. The validity of the method is checked by comparison with dynamic viscosity data available in literature. Comparison results are reported for many halocarbon refrigerants and for bis(difluoromethyl)ether (RE134) as well. Some exptl. data for **azeotropic** and non-**azeotropic** binary mixts. have also been compared with the dynamic viscosity predicted with the present method and a simple mixing rule. The results of the comparisons give av. abs. deviations and max. abs. deviations compatible with engineering applications.
- IT 56-23-5, properties 67-66-3, R20, properties 74-87-3, R40, properties 75-09-2, R30, properties 75-10-5, 75-69-4 75-71-8 75-72-9  
, R13  
(relationship between dynamic viscosity and reduced temp. of

refrigerant fluids and their mixts. in liq. phase)

RN 56-23-5 HCA

CN Methane, tetrachloro- (9CI) (CA INDEX NAME)



RN 67-66-3 HCA

CN Methane, trichloro- (9CI) (CA INDEX NAME)



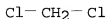
RN 74-87-3 HCA

CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)



RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)



RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-69-4 HCA

CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-71-8 HCA

CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-72-9 HCA  
 CN Methane, chlorotrifluoro- (8CI, 9CI) (CA INDEX NAME)



CC 65-6 (General Physical Chemistry)  
 Section cross-reference(s): 48, 68

IT **Azeotropes**

Liquid mixtures

Refrigerants

Viscosity

(relationship between dynamic viscosity and reduced temp. of refrigerant fluids and their mixts. in liq. phase)

IT 56-23-5, properties 67-66-3, R20, properties 74-87-3, R40, properties 75-00-3, R160 75-09-2, R30, properties 75-10-5 75-37-6, R152a 75-43-4, R21 75-45-6 75-46-7 75-63-8, R13B1 75-68-3, R142b 75-69-4 75-71-8 75-72-9, R13 75-88-7, R133a 76-13-1, R113 76-14-2, R114 76-15-3, R115 306-83-2, R123 354-23-4, R123a 354-33-6, R125 420-46-2, R143a 593-70-4, R31 811-97-2, R134a 1691-17-4, RE134 1717-00-6, R141b 2837-89-0, R124 (relationship between dynamic viscosity and reduced temp. of refrigerant fluids and their mixts. in liq. phase)

L14 ANSWER 6 OF 9 HCA COPYRIGHT 2002 ACS

122:217133 Optimization of the compositions for CFC alternative mixture refrigerants. Du, Liangui; Wang, Wenchuan; Zheng, Danxing; Fu, Jufu (Dep. Chem. Eng., Beijing Univ. Chem. Technology, Beijing, 100029, Peop. Rep. China). Chinese Journal of Chemical Engineering, 3(1), 32-8 (English) 1995. CODEN: CJCEEB. ISSN: 1004-9541. Publisher: Chemical Industry Press.

AB In this work, eight commonly used and recently developed cubic equations of state (EOSs) are extensively tested for the calcn. of thermodyn. properties, including vapor pressure, vapor and liq. densities, and heat of vaporization for 26 pure chlorofluorocarbons (CFCs) and their alternatives. The modified Du-Guo EOS is recommended for the vapor-liq. equil. calcns. of mixts. for its good accuracy. A method for the development of the optimized mixt. compns. of CFC alternatives is proposed by using minimization of

deviations between the vapor pressures of the CFCs and the alternative mixts. of interest. As examples, the binary mixts. R22-R142b and R22-R152a, and the ternary mixt. R22-R142b-R152a are tested. The results show that the vapor pressure of R12 can be well duplicated by a mixed refrigerant with the optimized compn. On the other hand, the deviations in the heat of vaporization are .apprx.10%. Moreover, all the mixts. discussed here are near **azeotropic** and are promising refrigerants to replace R12, as far as their thermodyn. properties are concerned.

- IT 56-23-5, Carbon tetrachloride, uses 67-66-3,  
 Chloroform, uses 74-87-3, Chloromethane, uses  
 75-09-2, **Methylene chloride**, uses  
 75-10-5 75-69-4, Trichlorofluoromethane  
 75-71-8, Dichlorodifluoromethane 75-72-9,  
 Chlorotrifluoromethane  
 (thermodyn. properties and the optimization of compns. for CFC  
 alternative mixt. refrigerants)
- RN 56-23-5 HCA  
 CN Methane, tetrachloro- (9CI) (CA INDEX NAME)



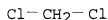
- RN 67-66-3 HCA  
 CN Methane, trichloro- (9CI) (CA INDEX NAME)



- RN 74-87-3 HCA  
 CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)



- RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)



- RN 75-10-5 HCA  
 CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-69-4 HCA  
 CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-71-8 HCA  
 CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-72-9 HCA  
 CN Methane, chlorotrifluoro- (8CI, 9CI) (CA INDEX NAME)



CC 45-5 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
 Section cross-reference(s): 69  
 IT 56-23-5, Carbon tetrachloride, uses 67-66-3,  
 Chloroform, uses 71-55-6, Methylchloroform 74-87-3,  
 Chloromethane, uses 75-00-3, Chloroethane 75-09-2,  
**Methylene chloride**, uses 75-10-5  
 75-34-3, 1,1-Dichloroethane 75-37-6, 1,1-Difluoroethane 75-43-4,  
 Dichlorodifluoromethane 75-45-6, Chlorodifluoromethane 75-46-7,  
 Fluoroform 75-68-3, 1-Chloro-1,1-difluoroethane 75-69-4,  
 Trichlorofluoromethane 75-71-8, Dichlorodifluoromethane  
 75-72-9, Chlorotrifluoromethane 75-73-0, Carbon  
 tetrafluoride 76-13-1, 1,1,2-Trichloro-1,2,2-trifluoroethane  
 76-14-2, 1,2-Dichloro-1,1,2,2-tetrafluoroethane 76-15-3 76-16-4,  
 Perfluoroethane 107-06-2, 1,2-Dichloroethane, uses 353-36-6,  
 Fluoroethane 374-07-2, 1,1-Dichloro-1,2,2,2-tetrafluoroethane  
 420-46-2, Methylfluoroform 593-53-3, Fluoromethane  
 (thermodn. properties and the optimization of compns. for CFC  
 alternative mixt. refrigerants)

L14 ANSWER 7 OF 9 HCA COPYRIGHT 2002 ACS  
 83:178038 Vapor pressures and critical points of liquids. V.

Halogenated methanes. (Engineering Sciences Data Unit, London, Engl.). Eng. Sci. Data Item, 75010, 29 pp. (English) 1975. CODEN: ESDIB8.

AB The vapor pressure, b.p., and crit. point of twenty-two halomethanes and 1:1 CHF<sub>3</sub>-ClCF<sub>3</sub> were listed.  
 IT 56-23-5, properties 67-66-3, properties  
 74-87-3, 75-09-2 75-10-5 75-69-4  
 75-71-8 75-72-9

(b.p., vapor pressure, and critical const. of)

RN 56-23-5 HCA

CN Methane, tetrachloro- (9CI) (CA INDEX NAME)



RN 67-66-3 HCA

CN Methane, trichloro- (9CI) (CA INDEX NAME)



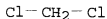
RN 74-87-3 HCA

CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)



RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)



RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-69-4 HCA

CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-71-8 HCA  
 CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-72-9 HCA  
 CN Methane, chlorotrifluoro- (8CI, 9CI) (CA INDEX NAME)



CC 22-8 (Physical Organic Chemistry)  
 Section cross-reference(s): 65, 48, 69, 68  
 IT Methane, trifluoro-, 1:1-**azeotrope** with  
 chlorotrifluoromethane  
 (b.p., vapor pressure, and critical const. of)  
 IT 56-23-5, properties 67-66-3, properties 74-83-9  
 74-87-3 74-88-4 74-95-3 74-97-5 75-09-2  
 75-10-5 75-25-2 75-43-4 75-45-6 75-46-7 75-61-6  
 75-62-7 75-63-8 75-69-4 75-71-8  
 75-72-9 75-73-0 353-59-3 593-53-3  
 (b.p., vapor pressure, and critical const. of)

L14 ANSWER 8 OF 9 HCA COPYRIGHT 2002 ACS  
 77:164010 Recovery and separation of perhalogenated fluorocarbons.  
 Ruehlen, Forrest N. (Phillips Petroleum Co.). U.S. US 3686082  
 19720822, 6 pp. (English). CODEN: USXXAM. APPLICATION: US  
 1970-15118 19700227.

AB The sepn. of electrofluorination products of CH<sub>2</sub>ClCH<sub>2</sub>Cl (I) was  
 improved by perchlorination. Thus, I was electrochem. fluorinated  
 at 95.degree. in an electrolyte of approx. compn. KF-2HF to give 7  
 chlorofluoroethanes. Chlori-nation of these gave a mixt. of  
 CClF<sub>2</sub>CF<sub>3</sub>, CClF<sub>2</sub>CClF<sub>2</sub>, CCl<sub>2</sub>-FCClF<sub>2</sub>, and CCl<sub>2</sub>FCCl<sub>2</sub>F, which was sepd.  
 by fractional **distn.** MeCl was fluorinated and chlorinated  
 similarly.



IT 75-10-5 75-69-4 75-71-8 75-72-9  
 (chloromethane fluorination product)  
 RN 75-10-5 HCA  
 CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-69-4 HCA  
 CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-71-8 HCA  
 CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



RN 75-72-9 HCA  
 CN Methane, chlorotrifluoro- (8CI, 9CI) (CA INDEX NAME)



IT 74-87-3  
 (fluorination of, electrochem.)  
 RN 74-87-3 HCA  
 CN Methane, chloro- (8CI, 9CI) (CA INDEX NAME)



IT 75-09-2P  
 (prepn. of)  
 RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IC B01J; B01K; C07C  
NCL 204059000  
CC 23-3 (Aliphatic Compounds)  
IT 75-10-5 75-43-4 75-45-6 75-46-7 75-69-4  
75-71-8 75-72-9 75-73-0 593-53-3 593-70-4  
(chloromethane fluorination product)  
IT 74-87-3 107-06-2  
(fluorination of, electrochem.)  
IT 75-09-2P  
(prepn. of)

L14 ANSWER 9 OF 9 HCA COPYRIGHT 2002 ACS

70:51382 Thermal conductivity of liquid refrigerants measured by an unsteady-state hot wire method. II. Tauscher, Willy A. (Eidg. Tech. Hochsch., Zurich, Switz.). Kaelte- tech.-Klim., 20(9), 287-90 (German) 1968. CODEN: KAKLBQ.

AB By using a previously reported hot wire method (T., 1967), the thermal cond. of 9 chlorofluoromethanes, of 5 chlorofluoroethanes, and of 5 azeotropic mixts. of these materials with SF<sub>6</sub> were measured in the range -125.degree. to 100.degree.. The cond. curves of the CH<sub>4</sub> derivs. could be represented within 2% by a simple empirical equation. Cond. of the C<sub>2</sub>H<sub>6</sub> derivs. could likewise be fitted within 1% by a sep. but similar equation. A log-log plot of thermal cond. vs. liq. d. gave a family of straight lines with slope of 1.95 +/- 10%. For the azeotropic mixts., deviations between calcd. and measured conds. were smaller when based on wt. rather than moles. Correction factors calcd. for a linear mixing equation (.lambda.mixt. = w1 .lambda.1 + w2.lambda.2) ranged 0.4-7.2%.

IT 75-09-2 75-10-5  
(thermal cond. of)  
RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IT 75-71-8  
(thermal cond. of difluoroethane and)  
RN 75-71-8 HCA  
CN Methane, dichlorodifluoro- (8CI, 9CI) (CA INDEX NAME)



CC 69 (Thermodynamics, Thermochemistry, and Thermal Properties)  
 IT 75-09-2 75-10-5 75-37-6 75-88-7 115-25-3  
 124-73-2 355-68-0 421-06-7 593-70-4 661-97-2 2268-46-4  
 4259-43-2  
 (thermal cond. of)  
 IT 75-71-8  
 (thermal cond. of difluoroethane and)

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L15 ANSWER 1 OF 19 HCA COPYRIGHT 2002 ACS

136:281151 Liquid-phase fluorination process for the manufacture of difluoromethane from dichloromethane and hydrogen fluoride with the concurrent feeding of a vaporized and superheated recycle stream of process reactants into the reactor. Cerri, Gustavo; Young, Frank Peter; Keeler, David William; Hunt, Maurice William (Honeywell International Inc., USA). PCT Int. Appl. WO 2002026672 A2 20020404, 12 pp. DESIGNATED STATES: W: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG, TR. (English). CODEN: PIXXD2. APPLICATION: WO 2001-US29736 20010924. PRIORITY: US 2000-671922 20000928.

AB A liq.-phase fluorination process for producing difluoromethane without corrosion is presented which comprises: (a) reacting methylene chloride and hydrogen fluoride in a reactor made of a fluorinated polymer in the presence of a fluorination catalyst to produce a reaction product; and (b) concurrently feeding a vaporized and superheated recycle stream of process reactants into the reactor.  
 IT 75-09-2, Dichloromethane, reactions  
 (lig.-phase fluorination process for the manuf. of difluoromethane from dichloromethane and hydrogen fluoride with the concurrent feeding of a vaporized and superheated recycle stream of process reactants into the reactor)  
 RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

- IC ICM C07C017-20
- ICS C07C019-08
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 47, 48
- ST **difluoromethane** manuf **dichloromethane**  
fluorination; fluoropolymer reactor **difluoromethane** manuf  
**dichloromethane** fluorination
- IT **Distillation**  
(in a liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride)
- IT Fluoropolymers, uses  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride in a reactor made of)
- IT **Distillation** columns  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride using)
- IT Ejectors  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride where the recycle stream is fed into the  
reactor using)
- IT Fluorination  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride with the concurrent feeding of a vaporized and  
superheated recycle stream of process reactants into the reactor)
- IT Fluoropolymers, uses  
(pipe lining; liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride with the concurrent feeding of a vaporized and  
superheated recycle stream of process reactants into the reactor)
- IT Distributing apparatus  
(spargers; liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride where the recycle stream is fed into the  
reactor using)
- IT 7647-01-0P, Hydrogen chloride, preparation  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride with the concurrent feeding of a vaporized and  
superheated recycle stream of process reactants into the reactor)
- IT 593-70-4P, Chlorofluoromethane  
(liq.-phase fluorination process for the manuf. of  
**difluoromethane** from **dichloromethane** and  
hydrogen fluoride with the concurrent feeding of a vaporized and  
superheated recycle stream of process reactants into the reactor)
- IT 75-09-2, **Dichloromethane**, reactions 7664-39-3,  
Hydrogen fluoride, reactions

- (lig.-phase fluorination process for the manuf. of difluoromethane from dichloromethane and hydrogen fluoride with the concurrent feeding of a vaporized and superheated recycle stream of process reactants into the reactor)
- IT 9002-84-0, Polytetrafluoroethylene (pipe lining; lig.-phase fluorination process for the manuf. of difluoromethane from dichloromethane and hydrogen fluoride with the concurrent feeding of a vaporized and superheated recycle stream of process reactants into the reactor)
- L15 ANSWER 2 OF 19 HCA COPYRIGHT 2002 ACS
- 134:43713 Liquid-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion. Cerri, Gustavo; Hunt, Maurice William; Keeler, David William; Young, Frank Peter (USA). U.S. US 6166275 A 20001226, 8 pp., Cont.-in-part of U. S. Ser. 972,531, abandoned. (English). CODEN: USXXAM. APPLICATION: US 1999-398745 19990917. PRIORITY: US 1997-972531 19971118.
- AB A lig.-phase fluorination process for producing difluoromethane from dichloromethane and HF without corrosion is described. Methylene chloride and hydrogen fluoride are reacted in a reactor made of a fluorinated polymer to produce a reaction product while a vaporized and superheated recycle stream of process reactants is fed into the reactor. Process flow diagrams are presented.
- IT 75-10-5P, Difluoromethane (lig.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- RN 75-10-5 HCA
- CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH<sub>2</sub>-F
- IT 75-09-2, Dichloromethane, reactions (lig.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- RN 75-09-2 HCA
- CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)
- Cl-CH<sub>2</sub>-Cl
- IC ICM C07C017-08
- NCL 570167000
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes) Section cross-reference(s): 23, 47, 48
- ST difluoromethane manuf equipment corrosion inhibition; dichloromethane fluorination difluoromethane manuf equipment corrosion inhibition

- IT Fluoropolymers, uses  
(coating in fluorination reactors for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- IT Corrosion prevention  
(in a liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride by using reactors contg. a fluoropolymer)
- IT Fluorination  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- IT Distillation  
Distillation columns  
Evaporation  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion using)
- IT 593-70-4P, Chlorofluoromethane  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- IT 7647-01-0P, Hydrogen chloride, preparation  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- IT 75-10-5P, Difluoromethane  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- IT 75-09-2, Dichloromethane, reactions 7664-39-3,  
Hydrogen fluoride, reactions  
(liq.-phase fluorination process for producing difluoromethane from dichloromethane and hydrogen fluoride without equipment corrosion)
- L15 ANSWER 3 OF 19 HCA COPYRIGHT 2002 ACS  
133:165739 Azeotrope-like compositions of difluoromethane and chlorine. Pham, Hang Thanh; Singh, Rajiv R.; Smith, Addison M.; Wilson, David P.; Thomas, Raymond Hilton Percival; Cerri, Gustavo (Alliedsignal Inc., USA). U.S. US 6099694 A 20000808, 4 pp., Cont.-in-part of U.S. Ser. No. 868,399, abandoned. (English). CODEN: USXXAM. APPLICATION: US 1998-46095 19980323. PRIORITY: US 1996-PV20181 19960614; US 1997-868399 19970603.
- AB The flammability of difluoromethane and chlorine-contg. mixts. in a distn. column, e.g., for fluorination, is controlled by controlling the chlorine feed. The chlorine feed is controlled so that the concn. of chlorine relative to difluoromethane in the column is maintained <22 wt.% (the flammability threshold for chlorine in a difluoromethane /chlorine mixt.). Formation of a flammable difluoromethane

/chlorine mixt. is minimized or avoided. The process can be used in prepn. of **difluoromethane** in which **difluoromethane** is sepd. from unreacted starting materials such as **methylene chloride**, hydrogen fluoride and monochloromonofluoromethane in .gtoreq.1 **distn.** column.

IT 75-09-2, **Methylene chloride**, processes  
(HCC-30; flammability control of **azeotropic** compns. of **difluoromethane** and chlorine in **distn.** columns for fluorination)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5P, **Difluoromethane**  
(HFC-32; flammability control of **azeotropic** compns. of **difluoromethane** and chlorine in **distn.** columns for fluorination)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IC ICM B01D003-36

ICS B01D003-42; C07C017-386; C07C019-03

NCL 203003000

CC 48-8 (Unit Operations and Processes)

Section cross-reference(s): 45, 59

ST safety flammability control fluorination **distn** column;  
**difluoromethane** chlorine flammability control **distn** column safety

IT **Distillation**  
**Distillation** columns

Flammability

Fluorination

Fluorination catalysts

Safety

(flammability control of **azeotropic** compns. of **difluoromethane** and chlorine in **distn.** columns for fluorination)

IT Halides  
(flammability control of **azeotropic** compns. of **difluoromethane** and chlorine in **distn.** columns for fluorination)

IT Hydrocarbons, processes  
(fluoro; flammability control of **azeotropic** compns. of **difluoromethane** and chlorine in **distn.** columns for fluorination)

IT 75-09-2, **Methylene chloride**, processes  
(HCC-30; flammability control of **azeotropic** compns. of

- difluoromethane and chlorine in **distn.** columns  
for fluorination)
- IT 593-70-4, Chlorofluoromethane  
(HCFC-31; flammability control of **azeotropic** compns. of  
**difluoromethane** and chlorine in **distn.** columns  
for fluorination)
- IT 75-10-5P, **Difluoromethane**  
(HFC-32; flammability control of **azeotropic** compns. of  
**difluoromethane** and chlorine in **distn.** columns  
for fluorination)
- IT 7664-39-3, Hydrogen fluoride, processes 7782-50-5, Chlorine,  
processes  
(flammability control of **azeotropic** compns. of  
**difluoromethane** and chlorine in **distn.** columns  
for fluorination)
- L15 ANSWER 4 OF 19 HCA COPYRIGHT 2002 ACS
- 130:353929 Fluorination process and noncorroding fluoropolymer reactors  
and **distillation** units for the manufacture of  
**difluoromethane** from **dichloromethane** and hydrogen  
fluoride. Cerri, Gustavo; Hunt, Maurice William; Keeler, David W.;  
Young, Frank P. (Alliedsignal Inc., USA). PCT Int. Appl. WO 9925670  
A1 19990527, 17 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA,  
BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH,  
GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU,  
LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI,  
SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ,  
MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, CY, DE, DK,  
ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN,  
TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1998-US24661  
19981118. PRIORITY: US 1997-972531 19971118.
- AB A liq.-phase fluorination process for producing  
**difluoromethane** without app. corrosion comprises the  
SbCl5-catalyzed reaction of **methylene chloride**  
and hydrogen fluoride in a reactor and **distn.** units made  
of a noncorroding fluoropolymer (e.g., polytetrafluoroethylene) to  
produce a reaction product while a heated recycle stream of process  
reactants is fed into the reactor. Process flow diagrams are  
presented.
- IT 75-10-5P, **Difluoromethane**  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- RN 75-10-5 HCA
- CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH<sub>2</sub>-F
- IT 75-09-2P, **Methylene chloride**,  
preparation  
(fluorination process and noncorroding fluoropolymer reactors and



- distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)
- Cl-CH<sub>2</sub>-Cl
- IC ICM C07C017-20  
ICS C07C019-08
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 47, 48
- ST **difluoromethane** manuf **dichloromethane**  
fluorination fluoropolymer reactor corrosion inhibition
- IT **Distillation**  
Fluorination  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT Fluoropolymers, uses  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT **Distillation** columns  
(noncorroding fluoropolymer **distn.** units for the prepn.  
of **difluoromethane** from **dichloromethane** and  
hydrogen fluoride)
- IT 7647-01-0P, Hydrogen chloride, preparation  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT 7647-18-9, Antimony pentachloride  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT 9002-84-0, Ptfе  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT 75-10-5P, **Difluoromethane**  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT 593-70-4P, Chlorofluoromethane  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)
- IT 75-09-2P, **Methylene chloride**,  
preparation  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)

IT 7664-39-3, Hydrogen fluoride, reactions  
(fluorination process and noncorroding fluoropolymer reactors and  
**distn.** units for the prepn. of **difluoromethane**  
from **dichloromethane** and hydrogen fluoride)

L15 ANSWER 5 OF 19 HCA COPYRIGHT 2002 ACS

129:218222 Production of **difluoromethane**. Cerri, Gustavo;  
Kong, Kin Ching (AlliedSignal Inc., USA). U.S. US 5800682 A  
19980901, 4 pp. (English). CODEN: USXXAM. APPLICATION: US  
1996-731038 19961008.

AB In prodn. of **difluoromethane** (I) by fluorination of  
**dichloromethane** (II), built-up of chlorofluoromethane (III)  
in a **distn.** column for a product stream contg. I, II, III,  
and HF is prevented by withdrawing a III-contg. side-stream from the  
column. The side-stream is withdrawn at a rate such that an amt.  
greater than or equal to the amt. of III in the product stream is  
removed from the **distn.** column.

IT 75-09-2, processes  
(prodn. of **difluoromethane** refrigerant from)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5P, **Difluoromethane**  
(prodn. of **difluoromethane** refrigerant from  
**dichloromethane**)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IC ICM B01D003-00

ICS C07C017-383

NCL 203099000

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)

Section cross-reference(s): 48

ST **difluoromethane** manuf chlorofluoromethane withdrawal;  
refrigerant **difluoromethane** manuf

IT Refrigerants

(replacement; prodn. of **difluoromethane** as replacement)

IT 75-09-2, processes

(prodn. of **difluoromethane** refrigerant from)

IT 75-10-5P, **Difluoromethane**

(prodn. of **difluoromethane** refrigerant from  
**dichloromethane**)

IT 593-70-4, Chlorofluoromethane

(removal in prodn. of **difluoromethane** refrigerant from  
**dichloromethane**)

L15 ANSWER 6 OF 19 HCA COPYRIGHT 2002 ACS

128:192354 Process for producing **difluoromethane**. Tsuda, Takehide; Shibamura, Takashi; Yamada, Yasufu (Daikin Industries Ltd., Japan; Tsuda, Takehide; Shibamura, Takashi; Yamada, Yasufu). PCT Int. Appl. WO 9808789 A1 19980305, 20 pp. DESIGNATED STATES: W: AU, BR, CA, CN, JP, KR, US; RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. (Japanese). CODEN: PIXXD2. APPLICATION: WO 1997-JP2961 19970826. PRIORITY: JP 1996-225290 19960827.

AB This document discloses a process for refining **difluoromethane** by removing hydrogen fluoride from **difluoromethane**; said process comprises **distg.** a mixt. of **difluoromethane** and hydrogen fluoride and bringing an **azeotropic** mixt. of both compds. as a **distillate** into contact with sulfuric acid, whereby hydrogen fluoride is absorbed by sulfuric acid. This process gives pure **difluoromethane**.

IT 75-10-5P, **Difluoromethane**  
(process for producing and purifying **difluoromethane**)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IT 75-09-2, **Dichloromethane**, reactions  
(process for producing and purifying **difluoromethane**)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IC ICM C07C019-08  
ICS C07C017-20; C07C017-38

CC 23-3 (Aliphatic Compounds)

ST **difluoromethane** purifn

IT Purification

(process for producing and purifying **difluoromethane**)

IT 7664-93-9, Sulfuric acid, uses

(process for producing and purifying **difluoromethane**)

IT 75-10-5P, **Difluoromethane**

(process for producing and purifying **difluoromethane**)

IT 75-09-2, **Dichloromethane**, reactions

(process for producing and purifying **difluoromethane**)

IT 7664-39-3, Hydrogen fluoride, reactions

(process for producing and purifying **difluoromethane**)

L15 ANSWER 7 OF 19 HCA COPYRIGHT 2002 ACS

128:142335 Removal of water from hydrofluorination process streams containing fluoroalkanes and hydrogen fluoride by phase separation and purge. Ewing, Paul Nicholas; Bujac, Paul David Bernard;

Bonniface, David William (Imperial Chemical Industries PLC, UK; Ewing, Paul Nicholas; Bujac, Paul David Bernard; Bonniface, David William). PCT Int. Appl. WO 9806685 A1 19980219, 19 pp. DESIGNATED STATES: W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1997-GB2104 19970805. PRIORITY: GB 1996-16879 19960810.

AB Water generated as a byproduct is removed from hydrofluorination process streams contg. it, hydrofluorocarbons, and hydrogen fluoride (e.g., product streams from vapor-phase hydrofluorination processes used in the manuf. of 1,1,1,2-tetrafluoroethane, pentafluoroethane, or difluoromethane) by phase sepn. and purge of the aq. layer, thus either avoiding or minimizing **distn.** and its problems. Process flow diagrams are presented.

IT 75-10-5P, Difluoromethane  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and **distn.**)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IT 75-09-2, Dichloromethane, reactions  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and **distn.**)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IC ICM C07C017-38

ICS C07C017-21; C07C017-20; C07C017-361; C07C019-08

CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48

ST phase sepn water removal hydrofluorination process; fluoroalkane prepn water removal hydrofluorination process; **distn** fluoroalkane prepn water removal

IT Alkanes, preparation

Alkenes, preparation

(chloro; removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and **distn.**)

IT Alkanes, preparation

- (fluoro; removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- IT Hydrofluorination  
Phase separation  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- IT 7732-18-5P, Water, preparation  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- IT 75-10-5P, Difluoromethane 354-33-6P,  
Pentafluoroethane 811-97-2P, 1,1,1,2-Tetrafluoroethane  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- IT 7664-39-3, Hydrogen fluoride, reactions  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- IT 75-09-2, Dichloromethane, reactions 75-88-7,  
1,1,1-Trifluoro-2-chloroethane 79-01-6, Trichloroethylene,  
reactions 127-18-4, Perchloroethylene, reactions 462-51-1,  
Bisfluoromethyl ether  
(removal of water from hydrofluorination process streams contg. fluoroalkanes and hydrogen fluoride by phase sepn. and distn.)
- L15 ANSWER 8 OF 19 HCA COPYRIGHT 2002 ACS  
127:347906 Fluorination process for the preparation of  
difluoromethane from dichloromethane and hydrogen  
fluoride. Garrait, Dominique; Guiraud, Emmanuel (Elf Atochem S.A.,  
Fr.). Eur. Pat. Appl. EP 805136 A1 19971105, 9 pp. DESIGNATED  
STATES: R: BE, DE, ES, FR, GB, GR, IT, NL. (French). CODEN:  
EPXXDW. APPLICATION: EP 1997-400754 19970402. PRIORITY: FR  
1996-5369 19960429.
- AB Difluoromethane is prepd. by the fluorination of  
dichloromethane and hydrogen fluoride in the presence of  
chlorine and a fluorination catalyst. The reaction mixt. is  
distd. to produce a head product, contg. HCl and  
difluoromethane, and a bottoms product, contg. 90% of the  
nonreacted dichloromethane, hydrogen fluoride, and  
chlorofluoromethane, which bottoms product is recycled to the  
fluorination reactor. A process flow diagram is presented.
- IT 75-10-5P, Difluoromethane  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)
- RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IT 75-09-2, Dichloromethane, reactions  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)  
RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IC ICM C07C017-20  
ICS C07C019-08  
CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48  
ST methylene fluoride manuf; fluorination process  
manuf methylene fluoride  
IT Fluorination  
(gas-phase; prepn. of difluoromethane from  
dichloromethane and hydrogen fluoride via)  
IT 7647-01-0P, Hydrogen chloride, preparation  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)  
IT 7440-47-3, Chromium, uses  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)  
IT 75-10-5P, Difluoromethane  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)  
IT 593-70-4P, Chlorofluoromethane  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)  
IT 75-09-2, Dichloromethane, reactions 7664-39-3,  
Hydrogen fluoride, reactions 7782-50-5, Chlorine, reactions  
(fluorination process for the prepn. of difluoromethane  
from dichloromethane and hydrogen fluoride)

L15 ANSWER 9 OF 19 HCA COPYRIGHT 2002 ACS  
126:263837 Vapor-phase process and catalysts for the production of  
difluoromethane from hydrogen fluoride and  
dichloromethane. Clemmer, Paul Gene; Smith, Addison Miles;  
Tung, Hsueh Sung; Bass, John Stephen (Alliedsignal Inc., USA). PCT  
Int. Appl. WO 9711043 A1 19970327, 14 pp. DESIGNATED STATES: W:  
AL, AU, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR,  
LK, LR, LT, LV, MG, MK, MN, MW, MX, NO, NZ, PL, RO, SD, SG, SI, SK,  
TR, TT, UA, UZ, VN, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM; RW: AT, BE,  
BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FI, FR, GA, GB, GR, IE, IT,  
LU, MC, ML, MR, NE, NL, PT, SE, SN, TD, TG. (English). CODEN:  
PIXXD2. APPLICATION: WO 1996-US14734 19960913. PRIORITY: US  
1995-530649 19950920.

- AB **Diffluoromethane** (i.e., HFC-32; I) is prepd. in high yield and selectivity by: (A) preheating a mixt. of HF (II) and **Cl<sub>2</sub>CH<sub>2</sub>** (III) to form a vaporized and superheater compn.; (B) reacting this superheated compn. in the presence of a fluorination catalyst (e.g., Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) to form a product stream contg. **F<sub>2</sub>CH<sub>2</sub>**, **ClFCH<sub>2</sub>** (IV), **HCl** (V), **Cl<sub>2</sub>CH<sub>2</sub>**, and HF; (C) **distg.** the product stream to produce a high-boiling stream comprising II, III, and IV, and a low-boiling stream comprising I, II, and V; and (D) recovering substantially pure I from the low-boiling **distn.** fraction.
- IT **75-10-5P, Diffluoromethane**  
(vapor-phase process and catalysts for the prodn. of **diffluoromethane** from hydrogen fluoride and **dichloromethane**)
- RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

- IT **75-09-2, Dichloromethane, reactions**  
(vapor-phase process and catalysts for the prodn. of **diffluoromethane** from hydrogen fluoride and **dichloromethane**)
- RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

- IC ICM C07C019-08  
ICS C07C017-20
- CC 23-3 (Aliphatic Compounds)  
Section cross-reference(s): 45, 48, 67
- IT Fluorination catalysts  
(dichromium trioxide for the conversion of **dichloromethane** with hydrogen fluoride in the high-yield manuf. of **diffluoromethane**)
- IT Fluorination  
(vapor-phase; of **dichloromethane** with hydrogen fluoride in the high-yield manuf. of **diffluoromethane**)
- IT 593-70-4P, Chlorofluoromethane  
(vapor-phase process and catalysts for the prodn. of **diffluoromethane** from hydrogen fluoride and **dichloromethane**)
- IT 7647-01-0P, Hydrogen chloride, preparation  
(vapor-phase process and catalysts for the prodn. of **diffluoromethane** from hydrogen fluoride and **dichloromethane**)
- IT 1308-38-9, Dichromium trioxide, uses  
(vapor-phase process and catalysts for the prodn. of **diffluoromethane** from hydrogen fluoride and

- dichloromethane)  
IT 75-10-5P, Difluoromethane  
(vapor-phase process and catalysts for the prodn. of difluoromethane from hydrogen fluoride and dichloromethane)  
IT 75-09-2, Dichloromethane, reactions 7664-39-3,  
Hydrogen fluoride, reactions  
(vapor-phase process and catalysts for the prodn. of difluoromethane from hydrogen fluoride and dichloromethane)
- L15 ANSWER 10 OF 19 HCA COPYRIGHT 2002 ACS  
124:120721 Performance of a rectification column on the reactor in the liquid-phase synthesis of **difluoromethane**. Vinogradov, D. V.; Barabanov, V. G.; Khomutov, V. A. (RNTs "Prikl. Khim.", St. Petersburg, Russia). Zhurnal Prikladnoi Khimii (Sankt-Peterburg), 68(8), 1395-7 (Russian) 1995. CODEN: ZPKHAB. ISSN: 0044-4618. Publisher: Nauka.  
AB The NRTL correlation equil. parameters for binary systems are derived to calc. the performance of a **distn.** column installed in the reactor for a liq.-phase **CH<sub>2</sub>F<sub>2</sub>** synthesis. Vapor-liq. equil. for **CH<sub>2</sub>F<sub>2</sub>**-HF and ClFCH<sub>2</sub>-HF systems was studied exptl. at 10.degree.. The exptl. data were used to calc. the parameters of the column installed in the reactor.  
IT 75-10-5P, Difluoromethane  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)  
RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH<sub>2</sub>-F  
IT 75-09-2, Dichloromethane, reactions  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)  
RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)
- Cl-CH<sub>2</sub>-Cl  
CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes) Section cross-reference(s): 68  
ST **distn** column **difluoromethane** liq phase prepn; activity hydrogen fluoride **dichloromethane** chlorofluoromethane  
IT Activity  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)  
IT **Distillation** apparatus  
(column, performance of a **distn.** column installed in



- the reactor for the liq.-phase **difluoromethane** synthesis)
- IT 7647-18-9, Antimony pentachloride  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)
- IT 75-10-5P, **Difluoromethane**  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)
- IT 75-09-2, **Dichloromethane**, reactions 7664-39-3,  
Hydrogen fluoride, reactions  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)
- IT 593-70-4P, Chlorofluoromethane  
(performance of a **distn.** column installed in the reactor for the liq.-phase **difluoromethane** synthesis)
- L15 ANSWER 11 OF 19 HCA COPYRIGHT 2002 ACS  
123:86591 Hydrogen fluoride-fluorination process and trivalent chromium catalysts for the production of **difluoromethane** and **azeotropes** of dihalomethanes containing chlorine from **dichloromethane**. Furmanek, Paul S.; Glasscock, David A.; Keane, Michael, Jr.; Mahler, Barry A.; Rao, Velliur Nott Mallikarjuna (du Pont de Nemours, E. I., and Co., USA). PCT Int. Appl. WO 9512563 A1 19950511, 26 pp. DESIGNATED STATES: W: JP; RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. (English). CODEN: PIXXD2. APPLICATION: WO 1994-US12473 19941031. PRIORITY: US 1993-146334 19931101.
- AB **Difluoromethane** is prep'd. by contacting a gaseous mixt. contg. **CH2Cl2** and HF with a catalyst contg. a trivalent chromium comp'd. (e.g., **CrCl3**, fluorided **CrCl3**, etc.) supported on C (having an ash content of <0.5 %) at 180-375.degree.. The catalyst and temp. conditions of this process allow the concurrent reaction **CCl3CF3** with HF to form **CCl2FCF3**. **CH2ClF** and unreacted **CH2Cl2**, each of which may be recovered as an **azeotrope** with HF, may be recycled.
- IT 75-10-5P, **Difluoromethane**  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH<sub>2</sub>-F
- IT 75-09-2, **Dichloromethane**, reactions  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

- IC ICM C07C017-20  
ICS C07C019-08; C07C019-10
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)  
Section cross-reference(s): 23, 48, 67
- ST **methylene fluoride** prepn fluorination  
chloromethane; chromium catalyst fluorination **methylene chloride**
- IT Fluorination catalysts  
(carbon-supported trivalent chromium compds for conversion of **dichloromethane** with HF in manuf. of **difluoromethane**)
- IT Fluorination  
(of **dichloromethane** with HF in presence of carbon-supported trivalent chromium compds. in manuf. of **difluoromethane**)
- IT 354-58-5P, 1,1,1-Trichloro-2,2,2-trifluoroethane 374-07-2P,  
2,2-Dichloro-1,1,1,2-tetrafluoroethane  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- IT 593-70-4P, Chlorofluoromethane  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- IT 7440-44-0, Carbon, uses 7440-47-3D, Chromium, trivalent salts 7788-97-8, Chromium trifluoride 10025-73-7, Chromium trichloride 10025-73-7D, Chromium trichloride, fluorided derivs.  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- IT 75-10-5P, **Difluoromethane**  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)
- IT 75-09-2, **Dichloromethane**, reactions 7664-39-3,  
Hydrogen fluoride, reactions  
(hydrogen fluoride-fluorination process and trivalent chromium catalysts for the prodn. of **difluoromethane** and **azeotropes** of dihalomethanes contg. chlorine from **dichloromethane**)

- Hiromoto; Takahashi, Reiji; Nakajo, Tetsuo (Showa Denko KK, Japan).  
Jpn. Kokai Tokkyo Koho JP 07033691 A2 19950203 Heisei, 5 pp.  
(Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-180421 19930721.
- AB CH2CF2 (HFC-32) (I), which is a substitute for ozone-depleting  
CHClF2 (HCFC-22), is prepd. by **distn.** of a reaction  
product formed from **CH2Cl2** and HF. A product formed by  
reacting **CH2Cl2** with HF is introduced to a **distn.**  
tower to **distill** off HCl from the top of the tower and  
to sep. the side-cut fraction mainly contg. I and a bottoms liq.  
consisting of **CH2Cl2**, CH2ClF, and HF and the side-cut  
fraction is introduced to a sep. purifn. step to recover I while the  
bottoms liq. is fed to a reactor. I is efficiently prepd. by using  
a simple app., wherein a single **distn.** tower separates the  
reaction product and recovers the byproduct HCl, and a combination  
of the bottoms liq. with replenished HF and **CH2Cl2** preps.  
a reaction raw material. This process is based on the finding that  
no **azeotrope** is formed for the I-HCl, I-HF, and HF-HCl  
system, whereas the CH2ClF-HF and CH2Cl-HF form min.  
**azeotropes.**
- IT 75-10-5P, Difluoromethane  
(purifn. of difluoromethane by **distn.** of  
reaction product from **methylene chloride** and  
hydrofluoric acid)
- RN 75-10-5 HCA  
CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH2-F
- IT 75-09-2, Dichloromethane, processes  
(purifn. of difluoromethane by **distn.** of  
reaction product from **methylene chloride** and  
hydrofluoric acid)
- RN 75-09-2 HCA  
CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)
- Cl-CH2-Cl
- IC ICM C07C019-08  
ICS C07C017-20
- CC 23-3 (Aliphatic Compounds)
- ST **difluoromethane** HFC32 purifn **distn**
- IT 75-10-5P, Difluoromethane  
(purifn. of difluoromethane by **distn.** of  
reaction product from **methylene chloride** and  
hydrofluoric acid)
- IT 75-09-2, Dichloromethane, processes 593-70-4,  
HCFC 31 7647-01-0, Hydrochloric acid, processes 7664-39-3,  
Hydrofluoric acid, processes  
(purifn. of difluoromethane by **distn.** of  
reaction product from **methylene chloride** and

hydrofluoric acid)

L15 ANSWER 13 OF 19 HCA COPYRIGHT 2002 ACS

122:105240 Manufacture of **difluoromethane**. Muramaki, Kazuo; Oono, Hiromoto; Nagayasu, Toshio (Showa Denko Kk, Japan). Jpn. Kokai Tokkyo Koho JP 06263658 A2 19940920 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1993-50954 19930311.

AB Title compd. (I) is manufd. from **dichloromethane** and HF by introducing the reaction products of **dichloromethane** and HF to the first **distn.** column for sepn. of HCl from the top and a fraction mainly consisting of I, chlorofluoromethane, **dichloromethane**, and HF from the bottom, introducing the bottom fraction to the second **distn.** column for withdrawal of a fraction mainly consisting of I from the top, forwarding the fraction to a sep. purifn. step to recover I, mixing the bottom from the second **distn.** column with dichloroethylene (sic) and HF to adjust the ratio and amt. of the reactants and feeding them to the reactor.

IT 75-09-2, **Dichloromethane**, reactions  
(fluorination with hydrogen fluoride to **difluoromethane**)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5P, **Difluoromethane**  
(prepn.; process and app. for)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IC ICM C07C019-08  
ICS C07C017-20; C07C017-38

CC 23-3 (Aliphatic Compounds)  
ST **difluoromethane** manuf; fluorination  
**dichloromethane** hydrogen fluoride

IT Fluorination  
(of **dichloromethane** with hydrogen fluoride to **difluoromethane**)

IT 7664-39-3, Hydrogen fluoride, reactions  
(fluorination of **dichloromethane** or **difluoromethane**)

IT 75-09-2, **Dichloromethane**, reactions  
(fluorination with hydrogen fluoride to **difluoromethane**)

IT 75-10-5P, **Difluoromethane**  
(prepn.; process and app. for)

L15 ANSWER 14 OF 19 HCA COPYRIGHT 2002 ACS

122:105239 Manufacture of **difluoromethane**. Muramaki, Kazuo;  
Oono, Hiromoto; Nagayasu, Toshio (Showa Denko Kk, Japan). Jpn.  
Kokai Tokkyo Koho JP 06263657 A2 19940920 Heisei, 5 pp. (Japanese).  
CODEN: JKXXAF. APPLICATION: JP 1993-50953 19930311.

AB Title compd. (I) is manufd. from **dichloromethane** and HF by  
introducing the reaction products of **dichloromethane** and  
HF to the first **distn.** column for sepn. of a main fraction  
contg. I and HCl and a bottom fraction contg.  
**dichloromethane**, chlorofluoromethane, and HF, introducing  
the main fraction to the second **distn.** column for removal  
of HCl from the top and withdrawal of a fraction mainly consisting  
of I from the bottom, forwarding the fraction from the bottom to a  
sep. purifn. step to recover I, and adding **dichloromethane**  
and HF to the bottom fraction from the first **distn.**  
column. to adjust the ratio and amt. of the reactants and feeding  
them to the reactor.

IT 75-09-2, **Dichloromethane**, reactions  
(fluorination with hydrogen fluoride to **difluoromethane**  
)

RN 75-09-2 HCA

CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5P, **Difluoromethane**  
(prepn.; process and app. for)

RN 75-10-5 HCA

CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

IC ICM C07C019-08

ICS C07C017-20; C07C017-38

CC 23-3 (Aliphatic Compounds)

ST **difluoromethane** manuf; fluorination

**dichloromethane** hydrogen fluoride

IT Fluorination

(of **dichloromethane** with hydrogen fluoride to  
**difluoromethane**)

IT 7664-39-3, Hydrogen fluoride, reactions  
(fluorination of **dichloromethane** to  
**difluoromethane**)

IT 75-09-2, **Dichloromethane**, reactions  
(fluorination with hydrogen fluoride to **difluoromethane**  
)

IT 75-10-5P, **Difluoromethane**  
(prepn.; process and app. for)

L15 ANSWER 15 OF 19 HCA COPYRIGHT 2002 ACS

- 120:167282 Method for removing hydrogen fluoride from halocarbon mixtures. Tsuda, Takehide; Matsumoto, Takeo; Tanaka, Yoshinori; Komatsu, Satoshi; Koyama, Satoshi (Daikin Industries, Ltd., Japan). PCT Int. Appl. WO 9321140 A1 19931028, 31 pp. DESIGNATED STATES: W: AU, BR, CA, JP, KR, RU, US; RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. (Japanese). CODEN: PIXXD2. APPLICATION: WO 1993-JP455 19930409. PRIORITY: JP 1992-92667 19920413; JP 1992-107656 19920427.
- AB The method comprises **distg.** the title mixt. to remove binary **azeotropic** mixts. composed of HF and R-30, HF and R-31, and HF and R-32 or sepg. the mixt. into an upper liq. rich in HF and a lower liq. poor in HF and **distg.** the resp. phase in a similar manner.
- IT 75-09-2P, R-30, preparation 75-10-5P, **Difluoromethane** (hydrogen fluoride removal from, by **distn.**)
- RN 75-09-2 HCA
- CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)
- Cl-CH<sub>2</sub>-Cl
- RN 75-10-5 HCA
- CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)
- F-CH<sub>2</sub>-F
- IC ICM C07C019-02  
ICS C07C019-08; C07C017-38
- CC 45-4 (Industrial Organic Chemicals, Leather, Fats, and Waxes)
- ST hydrogen fluoride removal **dichloromethane distn**;  
**difluoromethane distn** hydrogen fluoride removal;  
chlorofluoromethane **distn** hydrogen fluoride removal
- IT 75-09-2P, R-30, preparation 75-10-5P, **Difluoromethane** 593-70-4P, R-31 (hydrogen fluoride removal from, by **distn.**)
- L15 ANSWER 16 OF 19 HCA COPYRIGHT 2002 ACS
- 106:66701 A novel preparation of chlorofluoromethane. Anacona, Juan R.; Davies, Paul B.; Ferguson, Alan H. (Dep. Phys. Chem., Univ. Cambridge, Cambridge, CB2 1EP, UK). Chem. Ind. (London) (14), 490-1 (English) 1986. CODEN: CHINAG. ISSN: 0009-3068.
- AB The following lab. prepn. of high-purity CH<sub>2</sub>FC1 (as potential lasing gas) is given: dry **CH<sub>2</sub>Cl<sub>2</sub>** is introduced by a syringe into dry NaF/KF fluorinating mixt. at 400-500.degree. in a flask provided with a condenser at .apprx.-10.degree.. The products (**CH<sub>2</sub>F<sub>2</sub>** -CH<sub>2</sub>FC1 mixt.) are condensed in a cold trap at .apprx.-160.degree.. Several low-temp. vacuum **distns.** sep. the mixt. giving >90% pure CH<sub>2</sub>FC1.
- IT 75-09-2, **Dichloromethane**, reactions (fluorination of, in prepn. of pure chlorofluoromethane as lasing

gas)  
 RN 75-09-2 HCA  
 CN Methane, dichloro- (8CI, 9CI) (CA INDEX NAME)

Cl-CH<sub>2</sub>-Cl

IT 75-10-5, **Difluoromethane**  
 (sepn. of, from chlorofluoromethane, vacuum **distn.** for)  
 RN 75-10-5 HCA  
 CN Methane, difluoro- (8CI, 9CI) (CA INDEX NAME)

F-CH<sub>2</sub>-F

CC 23-3 (Aliphatic Compounds)  
 ST chlorofluoromethane prepn fluorination **dichloromethane**;  
 lasing gas chlorofluoromethane  
 IT Fluorination  
 (of **dichloromethane**, in chlorofluoromethane prepn.)  
 IT 75-09-2, **Dichloromethane**, reactions  
 (fluorination of, in prepn. of pure chlorofluoromethane as lasing  
 gas)  
 IT 7782-41-4  
 (fluorination, of **dichloromethane**, in  
 chlorofluoromethane prepn.)  
 IT 593-70-4P, Chlorofluoromethane  
 (prepn. of, as pure lasing gas, from **dichloromethane**)  
 IT 75-10-5, **Difluoromethane**  
 (sepn. of, from chlorofluoromethane, vacuum **distn.** for)

L15 ANSWER 17 OF 19 HCA COPYRIGHT 2002 ACS

63:45623 Original Reference No. 63:8167b-g Bromination of fluoro  
 alkanes. II. Fluoromethane and perfluoroethane. Tarr, A. M.;  
 Coomber, J. W.; Whittle, E. (Univ. Coll., Cardiff, UK). Trans.  
 Faraday Soc., 61(6), 1182-93 (English) 1965.  
 AB cf. CA 59, 8296c. The competitive vapor phase bromination of CH<sub>4</sub>  
 (I), MeF (II), CH<sub>2</sub>F<sub>2</sub> (III), CHF<sub>3</sub> (IV), and C<sub>2</sub>H<sub>5</sub>F (V) gave  
 kr/kf values of 0.56 +- 0.03 (2480 +- 40/RT), 2.01 +- 0.23  
 (780 +- 100/RT), 0.24 +- 0.01 (2000 +- 40/RT), 0.81 +- 0.05  
 (3040 +- 60/RT), and 8.88 + 0.85 (720 +- 90/RT), resp., leading  
 to activation energy (Eact) values of 103 +- 1, 105 +- 1, 2.2  
 +- 0.5, <103, <103, and <102 kcal./mole for D(Me-H), D(CF<sub>3</sub>-H),  
 D(CF<sub>3</sub>-H)-D(Me-H), D(H-CH<sub>2</sub>F), D(H-CHF<sub>2</sub>), and D(C<sub>2</sub>F<sub>5</sub>-H), resp. The  
 theoretical A factors for the reactions based on transition state  
 theory agree with the exptl. data. Since II and III are brominated  
 faster than I they are unsuitable bridges between I and IV, but  
 since both C<sub>2</sub>H<sub>6</sub> and V are brominated faster than I, V is a suitable  
 bridge compd. II was prepd. by the method of Edgell and Parts (CA  
 50, 6352e), III by treating **CH<sub>2</sub>Cl<sub>2</sub>** with SbCl<sub>5</sub> and anhyd.  
 HF in an autoclave at 150.degree. and purified from IV, CHF<sub>2</sub>Cl,  
 MeCl, and CH<sub>2</sub>FCl by low-temp. **distn.**, and V was made from

C2F5CO2H, CH2FBr from CH2FCO2H, and C2F5Br from C2F5CO2Ag and Br; all compds. were spectroscopically pure. In an app. described in part I (loc. cit.), 5-10 mm. Br and 120 mm. reactants was photolyzed until 1.5 mm. Br had reacted (about 1% of reactants consumed). The reaction mixt. was immediately removed and analyzed by chromatography or ir, of necessity measuring the proportions of brominated product in the presence of Br, HBr, and a large excess of unchanged reactants. Previous work indicating a large difference in the rate consts. for the bromination of I and IV was explained entirely in terms of a difference in Eact; apparently there is a difference in both A and E factors. The Eact for the abstraction of H by Br (increasing the no. of halogen atoms/mol.) passes through a min. along the I to IV series; the ratio of the rate consts. for abstraction of H by Br from II and I at 146.degree. is 11:1, which confirms the work of Fredricks and Tedder (CA 54, 9717i). The Eact for the abstraction of H.cntdot. from MeX by Br.cntdot. and CF3.cntdot. (and probably by Cl.cntdot. and Me.cntdot.) is reduced when X changes from H to a halogen, though the change is small, due probably to the weaker C-H bonds in MeX than in I so that the H abstraction is more exothermic for MeX. Passing from I to II to III there is a conflict between small bond energy decreases and polar effects, but from III to IV an increase in D-(C-H) combines with the polar effect to give a sharp increase in Eact. The polar effect is assocd. with repulsive forces in the transition state between X and RH and between XH and newly-formed R. Expts. show that the abstraction of H.cntdot. by CF3.cntdot. from HBr has a higher Eact than that of the corresponding reaction between Me.cntdot. and HBr, supporting the idea that there will be more repulsion in the IV transition state (due to the greater polarity of IV), thereby increasing the Eact. In the Me radical reaction, the lower Eact for attack on IV compared to I may be due to reduced repulsion between Me.cntdot. and IV owing to a redn. in electron density at the H of IV. The increase in reactivity down a series probably arises from a decrease in electron d. at the H under attack. The effect of change of force const. of the bond broken is not significant since this is probably a max. and the changes along the series are small (i.e., abstraction of H by Me.cntdot. is little influenced by polar effects). Thus the decrease in C-H bond energy of 10 kcal./mole from I to CHCl3 is probably caused by increasing stability of CC13 relative to Me. Since many heats of formation (Hf) of F compds. are uncertain (e.g., .DELTA.Hf(CF4) may be in error by 4-8 kcal./mole) the available value of .DELTA.Hf(CHF3) (Neugebauer and Margrave, CA 53, 845d) has not been used to calculate .DELTA.Hf(CF3) which is important in obtaining bond energies of the type D(R-CF3).

CC 32 (Physical Organic Chemistry)

L15 ANSWER 18 OF 19 HCA COPYRIGHT 2002 ACS

62:22275 Original Reference No. 62:3941a-c Fluorination of halogenated hydrocarbons. Anello, Louis G.; Woolf, Cyril (Allied Chemical Corp.). FR 1369782 19640814, 3 pp. (Unavailable). PRIORITY: US 19620926.

AB Fluoroalkanes contg. 1-4 C atoms are obtained by reaction of



straight-chain haloalkanes in the gas phase with HF in the presence of a Cr2O3 catalyst at 250-600.degree.. The process is particularly useful for the prepn. of CF4 from perchlorofluoromethanes. The catalyst is preferably employed without use of a support in granular or pellet form. Thus, 530 g. Cr(NO3)3.9H2O and 500 g. 28% aq. NH3 is added with agitation to 2000 cc. H2O at about 90.degree.. The resultant ppt. is filtered off, washed with H2O, partially dried at about 125.degree., and pressed into pellets. These pellets are then charged into a Ni reactor tube and heated at 370-400.degree. for about 4 hrs. in a current of inert gas until the effluent is free of H2O. This catalyst generally possesses a surface area of about 50 m.2/g. The fluorination reaction is carried out in the reactor tube in which the catalyst has been heat-treated. Thus, a charge of about 300 cc. catalyst was brought to .apprx.460.degree.. A mixt. of 1.41 moles CCl2F2 and 3.75 moles HF was passed over the catalyst at a rate sufficient to produce a contact time of .apprx.14 sec. The effluent gases were condensed in a trap cooled with liquid N. Titration of this condensate indicated the formation of 0.327 mole HCl. Fractional **distn.** yielded .apprx.1.35 moles CF4, b. -128.degree., and 0.06 mole CF3Cl, b. -81.degree., equivalent to yields of 96 and 4%, resp. Similarly, CCl4 gave 63% CF4 and 34% F3CCl, **CH2Cl2** gave 54% **CH2F2**, b. -50.degree., and 3% CH2ClF, b. -9.degree., and CHCl3 gave 47% Cl2FCH, b. 9.degree., 32% **F2CH2**, b. -40.degree., and 20% F3CH, b. -84.degree..

IC C07C

CC 33 (Aliphatic Compounds)

L15 ANSWER 19 OF 19 HCA COPYRIGHT 2002 ACS

54:6513 Original Reference No. 54:1295c-e Aliphatic fluorine compounds. Scherer, Otto; Hahn, Helmut; Kuhn, Heinrich (Farbwerke Hoechst Akt.-Ges. vorm. Meister Lucius & Bruning). DE 1020968 19571219 (Unavailable). APPLICATION: DE .

AB Chlorinated hydrocarbons were treated with HF in the presence of Sb catalysts and optionally chlorine and (or) As halides in Al reaction vessels. Thus, 20 kg. pentachloroethane, 5.5 kg. HF, 3.5 kg. SbF3, and 200 g. Cl was heated in an Al autoclave (30 l. capacity) to 140-50.degree./50 atm., the HCl allowed to escape during 10-15 hrs., and the resulting product **distd.** to give 48% trifluorodichloroethane and 43% difluorotrichloroethane, resp. Similarly were fluorinated hexachloroethane, **CH2Cl2** (to give **methylene fluoride**, b. -52.degree.), trichloroethylene, 2-fluoroheptachloro-propane, and 1,2,3,4-tetrafluorohexachlorobutane (to give 1,2,3,4-tetrachlorohexafluorobutane, b. 134-5.degree.).

NCL 120

CC 10B (Organic Chemistry: Aliphatic Compounds)

=&gt; file wpids

FILE 'WPIDS' ENTERED AT 12:08:15 ON 01 OCT 2002

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FILE LAST UPDATED: 26 SEP 2002 <20020926/UP>  
 MOST RECENT DERWENT UPDATE 200262 <200262/DW>  
 DERWENT WORLD PATENTS INDEX SUBSCRIBER FILE, COVERS 1963 TO DATE

=> d l21 1-4 max

L21 ANSWER 1 OF 4 WPIDS (C) 2002 THOMSON DERWENT

AN 2001-627597 [73] WPIDS

DNC C2001-187132

TI Purification of **difluoromethane** used as refrigerant, involves carrying out **extraction** treatment of **difluoromethane** and hydrogen fluoride followed by liquid separation and separating **difluoromethane** from **extractant** layer.

DC E16 G04 J07 J08

IN SUZUKI, Y; YANASE, K; YOKOYAMA, T

PA (ASAG) ASahi GLASS CO LTD

CYC 30

PI EP 1127863 A1 20010829 (200173)\* EN 7p C07C017-38  
 R: AL AT BE CH CY DE DK ES FI FR GB GR IE IT LI LT LU LV MC MK  
 NL PT RO SE SI TR

JP 2001233808 A 20010828 (200173) 5p C07C017-38

US 6297412 B1 20011002 (200173) C07C019-00

US 2001021793 A1 20010913 (200173) C07C017-38

CN 1310158 A 20010829 (200176) C07C019-08

KR 2001082755 A 20010830 (200215) C07C017-38

ADT EP 1127863 A1 EP 2001-103558 20010219; JP 2001233808 A JP 2000-44967  
 20000222; US 6297412 B1 US 2001-788591 20010221; US 2001021793 A1 US  
 2001-788591 20010221; CN 1310158 A CN 2001-104776 20010222; KR  
 2001082755 A KR 2001-8872 20010222

PRAI JP 2000-44967 20000222

IC ICM C07C017-38; C07C019-00; C07C019-08

ICS C07C017-20

AB EP 1127863 A UPAB: 20011211

NOVELTY - A mixture of **difluoromethane** and hydrogen fluoride is subjected to **extraction** treatment using an **extractant** chosen from **dichloromethane** or chlorofluoromethane followed by liquid separation to form **extractant** layer and hydrogen fluoride layer. The **extractant** layer comprises **difluoromethane** and **extractant**, from which **difluoromethane** is separated.

USE - For purification of **difluoromethane** used as refrigerant.

ADVANTAGE - High purity **difluoromethane** and HF can be efficiently **extracted** and separated. The separated HF can be reused by returning to reaction system for producing **difluoromethane** without separating **extractant**. The physical properties of the **extractants** used are similar to that of **difluoromethane** and show small mutual solubility

to HF and large mutual solubility to **difluoromethane**.  
Amount of **extractant** used is reduced.  
Dwg.0/0

TECH EP 1127863 A1 UPTX: 20011211

TECHNOLOGY FOCUS - ORGANIC CHEMISTRY - Preferred Composition: The proportion of HF in the mixture is 5-1000 weight parts (wt.pts) per 100 wt.pts of **difluoromethane** and the amount of **extractant** is 0.3-30 times (by molar ratio) to the amount of **difluoromethane**.

Preferred Process: Liquid separation is carried out at -40 to 50 degreesC and 0.1-3 MPa pressure. The **extractant** layer is **distilled** to separate **difluoromethane** and **extractant** is returned to the step of **extraction** treatment. The mixture contains reaction product obtained by fluorinating **dichloromethane** with hydrogen fluoride. The hydrogen fluoride layer is returned to the reaction step to obtain the mixture, without removing **extractant** and **difluoromethane**.

KW [1] 8406-0-0-0 CL PRD

FS CPI

FA AB; DCN

MC CPI: E10-H03A3; E11-Q01; G04-B01; J07-A08; J08-D06

CMC UPB 20011211

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
M720 M904 M905 N164 Q431 Q433  
DCN: R07374-K; R07374-P

L21 ANSWER 2 OF 4 WPIDS (C) 2002 THOMSON DERWENT

AN 1999-180460 [15] WPIDS

DNC C1999-052559

TI Separation of **difluoromethane** from halocarbon mixture -  
by contacting with hydrocarbon, oxygen-containing and-or  
chlorocarbon **extractive** agents followed by  
**extractive distillation**.

DC E16 L03

IN BOEHMER, S W; MAHLER, B A; MILLER, R N

PA (DUPO) DU PONT DE NEMOURS & CO E I

CYC 20

PI WO 9907660 A1 19990218 (199915)\* EN 28p C07C017-386  
RW: AT BE CH CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE  
W: JP US

EP 1003699 A1 20000531 (200031) EN C07C017-386  
R: DE FR GB IT NL

JP 2001513520 W 20010904 (200165) 34p C07C017-386

ADT WO 9907660 A1 WO 1998-US16689 19980812; EP 1003699 A1 EP 1998-939352  
19980812, WO 1998-US16689 19980812; JP 2001513520 W WO 1998-US16689  
19980812, JP 2000-507197 19980812

FDT EP 1003699 A1 Based on WO 9907660; JP 2001513520 W Based on WO  
9907660

PRAI US 1997-55502P 19970812

IC ICM C07C017-386

ICS C07C019-08

AB WO 9907660 A UPAB: 19990416  
 NOVELTY - Uses **extractive distillation** to separate **difluoromethane** from halocarbon mixtures.  
**DETAILED DESCRIPTION** - The process separates **difluoromethane** (HFC-32) from halocarbons comprising **difluoromethane** (HFC-32), chlorodifluoromethane (CFC-12), 1,1,1-trifluoroethane (HFC-143a), chloropentafluoroethane (CFC-115) and pentafluoroethane (HFC-125), by: (a) contacting the mixture with an **extractive** agent selected from: (1) hydrocarbon **extractive** agents comprising 5-9C hydrocarbons and b.pt. 30-155 deg. C.; (2) oxygen-containing **extractive** agents comprising alcohols of b.pt. 60-100 deg. C and of formula  $C_xH_{2x+1}OH$ , where  $x = 1-3$ , and ketones of b.pt. 50-110 deg. C and of formula  $CyH_{2y+1}COCzH_{2z+1}$ , where  $y$  and  $z$  each are 1 or more and their sum is 5 max; and/or (3) chlorocarbon **extractive** agents comprising chlorocarbons of b.pt. 39-150 deg. C and of formula  $CsH_{2s+t}Cl_t$ , where  $s = 1$  or  $2$ ,  $t = 2-4$ , to form a second mixture, (b) separating HFC-32 from at least one halocarbon of the second mixture by **extractive distillation** and (c) recovering HFC-32 free of at least one halocarbon, when the halocarbon is HFC-125, the chlorocarbon **extractive** agent is not **methylene chloride**.

Preferably the hydrocarbon **extractive** agent is 5-7C hydrocarbons of b.pt. 30-110 deg. C, and is n-pentane, 2-methylpentane, 3-methylpentane, cyclopentane, methylcyclopentane, n-hexane, cyclohexane or n-heptane. The oxygen-containing **extractive** agent is methanol, ethanol, propanol, isopropanol, propanone or butanone. The chlorocarbon **extractive** agent is **methylene chloride**.

The HFC-32 recovered from the second mixture contains less than 50 preferably less than 0.1 p.p.m. wt. halocarbon. The process further includes recycling at least part of the **extractive** agent obtained from the **extractive distillation** for use in preparation of the second mixture of the contacting step. The **extractive distillation** is carried out at 15-350 psia and reflux ratio of 1/1 to 10/1. The HFC-32 and halocarbon of the first mixture are an **azeotropic** composition.

USE - For use in **extraction** and purification of **difluoromethane** from halocarbon mixture.

ADVANTAGE - Provides more cost-effective and efficient separation and purification of **difluoromethane**.

DWG.1/1

FS CPI

FA AB; GI; DCN

MC CPI: E10-H03A3; E11-Q01; L04-X

DRN 0245-U; 0270-U; 0271-U; 0302-U; 0345-P; 0345-U; 0879-U; 0904-U;

0913-U; 1145-U; 1191-U

CMC UPB 19990424

M3 \*01\* H6 H602 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M720 M903 M904 M910 N163 N521 N522 N523 Q431 Q454

DCN: R00345-K; R00345-P

L21 ANSWER 3 OF 4 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1994-338218 [42] WPIDS  
 DNN N1994-265772 DNC C1994-153912  
 TI Prepn. of di fluoromethane - by **distn.** of reaction prod.  
 from reaction of di chloromethane and hydrogen.  
 DC E16 J07 X27  
 PA (SHOW) SHOWA DENKO KK  
 CYC 1  
 PI JP 06263658 A 19940920 (199442)\* 5p C07C019-08  
 ADT JP 06263658 A JP 1993-50954 19930311  
 PRAI JP 1993-50954 19930311  
 IC ICM C07C019-08  
 ICS C07C017-20; C07C017-38  
 AB JP 06263658 A UPAB: 19941212

**Difluoromethane** (I) is prepared by 1st **distillation** of the product obtd. by reaction of **dichloromethane** (II) with HF, bottom soln (III) which is including (I), chlorofluoromethane, **dichloromethane** and HF, is given. On the other hand HCl is **extracted** from the top.

By 2nd **distillation** of (III), (I) is **extracted** from the top.

USE/ADVANTAGE - (I) is a useful material instead of HCFC-22 (CHClF2) which destroys the ozone layer and which is used as a coolant in refrigerators and air conditioners. By this simple method (I) is given efficiently due to collection of side product (HCl) efficiently.

Dwg. 0/0

FS CPI EPI  
 FA AB; GI; DCN  
 MC CPI: E10-H03A3; J01-A02A; J07-A08; N01-C02; N03-D01  
 EPI: X27-F  
 DRN 0345-S; 1544-S; 1704-P; 1712-S; 1933-S  
 CMC UPB 19950207  
 M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424  
 M620 M720 M903 M904 N164 N209 N225 N309 N322 N441 N513 N514  
 N521 N522 Q433  
 DCN: R07374-P  
 M3 \*02\* A424 A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411  
 M730 M903 M910 Q421

L21 ANSWER 4 OF 4 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1994-338217 [42] WPIDS  
 DNN N1994-265771 DNC C1994-153911  
 TI Prepn. of di fluoromethane - by reaction of di chloromethane with  
 hydrogen chloride, followed by **distillation**.  
 DC E16 J07 X27  
 PA (SHOW) SHOWA DENKO KK  
 CYC 1  
 PI JP 06263657 A 19940920 (199442)\* 5p C07C019-08  
 ADT JP 06263657 A JP 1993-50953 19930311  
 PRAI JP 1993-50953 19930311

IC ICM C07C019-08  
 ICS C07C017-20; C07C017-38  
 AB JP 06263657 A UPAB: 19941212  
**Difluoromethane** (I) is prep'd. by 1st **distn.** of the prodn. of reaction of **dichloromethane** (II) with HF, an **extract** (III) which is including (I) and HCl.  
 By 2nd **distn.** of (III) HCl is **extracted** and (I) is given from the lower fraction.  
 USE/ADVANTAGE - (I) is a useful material instead of HFC-22 (CHClF2) which destroys the ozone layer and which is used as a coolant in refrigerators and room air conditions. By this simple apparatus (I) is given efficiently due to collection of side product (HCl) efficiently.  
 Dwg.1/1  
 FS CPI EPI  
 FA AB; GI; DCN  
 MC CPI: E10-H03A3; J01-A02A; J07-A08; N01-C02; N03-D01  
 EPI: X27-F  
 DRN 0345-S; 1544-S; 1704-P; 1712-S; 1933-S  
 CMC UPB 19950207  
 M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424  
 M620 M720 M740 M903 M904 N105 N164 N209 N225 N309 N322 N441  
 N513 N514 N521 N522 Q433  
 DCN: R07374-P  
 M3 \*02\* A424 A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411  
 M730 M903 M910 Q421

=> d 122 1-15 ti

- L22 ANSWER 1 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 TI Fluorination process for the preparation of **difluoromethane** comprises reacting **methylene chloride** with hydrogen fluoride in the presence of catalyst and superheated recycle stream in a reactor made of fluorinated polymer.
- L22 ANSWER 2 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 TI Liquid phase fluorination for producing hydrofluorocarbons involves reacting **methylene chloride**, hydrogen fluoride, and concurrently feeding a vaporized and superheated recycle stream of reactants to the reactor.
- L22 ANSWER 3 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 TI A hydrofluorination process esp. for the production of **difluoromethane**.
- L22 ANSWER 4 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 TI Reduction of amount of mono chloro-mono fluoro-methane in di fluoro-methane product stream - by **distillation** with removal of a side-stream containing mono chloro-mono fluoro-methane, useful in production of refrigerants.

- L22 ANSWER 5 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI **Azeotrope**-like compositions, useful as coolants and reactants in exothermic chlorination reactions - contain di fluoro-methane and chlorine.
- L22 ANSWER 6 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Di fluoromethane production for use in refrigeration and air conditioning - by gaseous phase reaction of **methylene chloride** with hydrogen fluoride in presence of chlorine and fluorination catalyst.
- L22 ANSWER 7 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Di fluoro methane prodn. from di chloro methane and hydrogen fluoride - by reacting the pre-heated starting mixt. in the presence of a fluorination catalyst and sepgg. the prod. stream by **distn.**.
- L22 ANSWER 8 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Di fluoromethane prodn. - by catalytic gas phase fluorination of **methylene chloride** with anhydrous hydrogen fluoride in presence of chlorine.
- L22 ANSWER 9 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Di fluoromethane prodn. - by catalytic gas phase fluorination of **methylene chloride** with anhydrous hydrofluoric acid using chromium catalyst.
- L22 ANSWER 10 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Prodn. of di fluoro-methane useful as refrigerant - by liq. phase reaction of **methylene chloride** with hydrogen fluoride in the presence of an antimony penta chloride catalyst.
- L22 ANSWER 11 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Sepn. of hydrogen fluoride and di fluoromethane - by **distn** . and/or fractional condensn..
- L22 ANSWER 12 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Di fluoromethane prodn., useful as chloro-fluoro-carbon replacement - by gas phase contact of di chloromethane and hydrogen fluoride over a carbon supported trivalent chromium catalyst, used as refrigerant.
- L22 ANSWER 13 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI Purificn. of di fluoromethane to remove acid - comprises introducing **distilled** prod. into **distn.** column, gas side cutting obtd. heavy component and contacting with aq. alkali soln..
- L22 ANSWER 14 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
TI **Azeotropic** mixt. of hydrogen fluoride and di chloromethane, di fluoromethane or chloro-fluoromethane - used to remove hydrogen fluoride simply, without causing pollution.

L22 ANSWER 15 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 TI Aerosol propellant contg. chloro-di fluoro-methane - and di methyl ether, with addn. of di chloro-methane, having vapour pressure 50 to 60 psig.

=> d 122 1,2,3,4,6,7,8,9,10,11,12,14 max

L22 ANSWER 1 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 2002-281318 [32] WPIDS

DNC C2002-082778

TI Fluorination process for the preparation of **difluoromethane** comprises reacting **methylene chloride** with hydrogen fluoride in the presence of catalyst and superheated recycle stream in a reactor made of fluorinated polymer.

DC E16

IN CERRI, G; HUNT, M W; KEELER, D W; YOUNG, F P

PA (HONE) HONEYWELL INT INC

CYC 90

PI WO 2002026672 A2 20020404 (200232)\* EN 12p C07C017-20

RW: AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC

MW MZ NL OA PT SD SE SL SZ TR TZ UG ZW

W: AE AL AM AT AU AZ BA BB BG BR BY CA CH CN CR CU CZ DE DK DM

EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ

LC LK LR LS LT LU LV MA MD MG MK MN MW MX NO NZ PL PT RO RU

SD SE SG SI SK SL TJ TM TR TT TZ UA UG UZ VN YU ZA ZW

AU 2001092985 A 20020408 (200252) C07C017-20

ADT WO 2002026672 A2 WO 2001-US29736 20010924; AU 2001092985 A AU

2001-92985 20010924

FDT AU 2001092985 A Based on WO 200226672

PRAI US 2000-671922 20000928

IC ICM C07C017-20

ICS C07C019-08

AB WO 200226672 A UPAB: 20020521

NOVELTY - **Methylene chloride** and hydrogen fluoride are reacted in the presence of a fluorination catalyst in a reactor made of fluorinated polymer to form a reaction product. A vaporized and superheated recycle stream of process reactants is fed concurrently into the reactor.

USE - The process is a hydrofluorination process for the production of **difluoromethane** (HFC-32).

ADVANTAGE - The fluorination process exhibits efficient heat transfer and high productivity without corrosion in the reactor system.

Dwg.0/0

TECH WO 200226672 A2UPTX: 20020521

TECHNOLOGY FOCUS - ORGANIC CHEMISTRY - Preferred Method: The recycle stream feed process involves:

(i) **distilling** the reaction product to produce a column bottoms product comprising HF, **methylene chloride** and chlorofluoromethane and a column overhead product comprising HCl, **difluoromethane**, chlorofluoromethane,



**methylene chloride** and HF;

(ii) withdrawing a vapor sidestream from an intermediate part of the **distillation** column;

(iii) condensing the vapor sidestream to form a liquid;

(iv) vaporizing the liquid from (iii);

(v) superheating the vapor; and

(vi) recycling the superheated vapor to the reactor.

In step (iv), partial vaporization may be carried out to produce a vapor portion (which is subsequently superheated) and liquid portion, both of which are recycled. The recycle stream is superheated to a temperature of 10-150 degreesC above the reactor temperature. The vaporization and superheating processes may be carried out in a single step. The recycle stream is fed into the reactor through a sparger or eductor.

KW [1] 8406-0-0-0 CL PRD; 354-0-0-0 CL; 219-0-0-0 CL; 27-0-0-0 CL

FS CPI

FA AB; DCN

MC CPI: E10-H03A3; E11-H; N03-H; N04-D01; N07-D09

DRN 0345-S; 0345-U; 1712-S; 1712-U

CMC UPB 20020521

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424  
M620 M720 M904 M905 N209 N225 N309 N322 N441 N513 N522

DCN: R07374-K; R07374-P  
M3 \*02\* A351 A940 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411  
M730 M904 M905 Q421  
DCN: R04326-K; R04326-C

M3 \*03\* C009 C100 C101 C730 C800 C801 C804 C805 C806 C807 M411 M730  
M904 M905 M910

DCN: R01712-K; R01712-S  
M3 \*04\* H6 H602 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
M730 M904 M905 M910  
DCN: R00345-K; R00345-S

L22 ANSWER 2 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 2001-167692 [17] WPIDS

CR 1999-357600 [30]

DNC C2001-049926

TI Liquid phase fluorination for producing hydrofluorocarbons involves reacting **methylene chloride**, hydrogen fluoride, and concurrently feeding a vaporized and superheated recycle stream of reactants to the reactor.

DC A97 E16

IN CERRI, G; HUNT, M W; KEELER, D W; YOUNG, F P

PA (CERR-I) CERRI G; (HUNT-I) HUNT M W; (KEEL-I) KEELER D W; (YOUN-I) YOUNG F P

CYC 1

PI US 6166275 A 20001226 (200117)\* 8p C07C017-08

ADT US 6166275 A CIP of US 1997-972531 19971118, US 1999-398745 19990917

PRAI US 1999-398745 19990917; US 1997-972531 19971118

IC ICM C07C017-08

AB US 6166275 A UPAB: 20010328

NOVELTY - Providing a liquid phase fluorination process for

producing **difluoromethane** that exhibits efficient heat transfer and high productivity and that eliminates corrosion in the reactor system.

**DETAILED DESCRIPTION** - A liquid phase fluorination comprises reacting **methylene chloride** (HCC-30), hydrogen fluoride, and fluorination catalyst in a fluorinated polymer reactor. The reaction product was **distilled** in a first **distillation** column to produce a first column bottoms product and a first column overhead product. The first column bottoms product is recycled to the reactor. The first column overhead product comprises hydrogen chloride (HCl), **difluoromethane** (**CH<sub>2</sub>F<sub>2</sub>**), monochloromonofluoromethane (HCFC-31), HCC-30, and hydrogen fluoride (HF). The first column overhead product is **distilled** in a second **distillation** column to produce a second column bottoms product comprising HCFC-31, HCC-30, and HF, and a second column overhead product comprising **CH<sub>2</sub>F<sub>2</sub>** and HCl. The second column bottoms product was vaporized and superheated, and was recycled to the reactor.

**INDEPENDENT CLAIMS** are also claimed for the process.

**USE** - The method is useful for the production of hydrofluorocarbons (HFC's), e.g. **difluoromethane**.

**ADVANTAGE** - The method produces HFC's that exhibits efficient heat transfer and high productivity and eliminates corrosion in the reactor system.

Dwg.0/3

TECH US 6166275 A UPTX: 20010328

**TECHNOLOGY FOCUS** - **CHEMICAL ENGINEERING** - Preferred Method: The first and second bottom products are superheated to 100-200 degrees C, before they are recycled to the reactor. The liquid stream is partially vaporized to produce vapor and liquid portions. The vapor portion is superheated, and the superheated vapor portion and the liquid portion are recycled to the reactor.

KW [1] 8406-0-0-0 CL PRD; 131815-0-0-0 CL PRD; 354-0-0-0 CL; 27-0-0-0 CL; 219-0-0-0 CL

FS CPI

FA AB; DCN

MC CPI: A04-E10; A12-W11; E10-H03A3; E10-H03B2; N04-D01

DRN 0345-S; 0345-U; 1712-S; 1712-U

PLE UPA 20010418

[1.1] 018; P0500 F- 7A

[1.2] 018; Q9999 Q6973 Q6939; ND01; K9416

CMC UPB 20010418

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424 M620 M720 M740 M904 M905 N209 N224 N225 N309 N322 N441 N513 Q130

DCN: R07374-K; R07374-P

M3 \*02\* H6 H601 H602 H684 M280 M311 M321 M342 M363 M391 M416 M424 M620 M720 M740 M904 M905 N209 N224 N225 N309 N322 N441 N513 Q130

DCN: R09219-K; R09219-P

M3 \*03\* A351 A940 C017 C100 C730 C801 C803 C804 C805 C806 C807 M411

M730 M904 M905 Q421  
 DCN: R04326-K; R04326-C  
 M3 \*04\* H6 H602 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M730 M904 M905 M910  
 DCN: R00345-K; R00345-S  
 M3 \*05\* C009 C100 C101 C730 C800 C801 C804 C805 C806 C807 M411 M730  
 M904 M905 M910  
 DCN: R01712-K; R01712-S

L22 ANSWER 3 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1999-357600 [30] WPIDS  
 CR 2001-167692 [06]  
 DNC C1999-105778  
 TI A hydrofluorination process esp. for the production of  
**difluoromethane.**  
 DC A14 A97 E16  
 IN CERRI, G; HUNT, M W; KEELER, D W; YOUNG, F P  
 PA (ALLC) ALLIED-SIGNAL INC  
 CYC 80  
 PI WO 9925670 A1 19990527 (199930)\* EN 17p C07C017-20  
 RW: AT BE CH CY DE DK EA ES FI FR GB GH GM GR IE IT KE LS LU MC  
 MW NL OA PT SD SE SZ UG ZW  
 W: AL AM AT AU AZ BA BB BG BR BY CA CH CN CU CZ DE DK EE ES FI  
 GB GE GH GM HU ID IL IS JP KE KG KP KR KZ LC LK LR LS LT LU  
 LV MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ  
 TM TR TT UA UG UZ VN YU ZW  
 AU 9914193 A 19990607 (199943)  
 EP 1042256 A1 20001011 (200052) EN C07C017-20  
 R: BE DE FR GB IT NL  
 CN 1285812 A 20010228 (200131) C07C017-20  
 KR 2001032248 A 20010416 (200163) C07C017-20  
 MX 2000004859 A1 20010301 (200170) C07C017-20  
 BR 9814979 A 20011120 (200202) C07C017-20  
 JP 2001523652 W 20011127 (200204) 15p C07C017-20  
 NZ 504616 A 20020201 (200214) C07C017-20  
 ADT WO 9925670 A1 WO 1998-US24661 19981118; AU 9914193 A AU 1999-14193  
 19981118; EP 1042256 A1 EP 1998-958082 19981118, WO 1998-US24661  
 19981118; CN 1285812 A CN 1998-813046 19981118; KR 2001032248 A KR  
 2000-705451 20000518; MX 2000004859 A1 MX 2000-4859 20000518; BR  
 9814979 A BR 1998-14979 19981118, WO 1998-US24661 19981118; JP  
 2001523652 W WO 1998-US24661 19981118, JP 2000-521057 19981118; NZ  
 504616 A NZ 1998-504616 19981118, WO 1998-US24661 19981118  
 FDT AU 9914193 A Based on WO 9925670; EP 1042256 A1 Based on WO 9925670;  
 BR 9814979 A Based on WO 9925670; JP 2001523652 W Based on WO  
 9925670; NZ 504616 A Based on WO 9925670  
 PRAI US 1997-972531 19971118  
 IC ICM C07C017-20  
 ICS C07C017-383; C07C019-08  
 AB WO 9925670 A UPAB: 20020301  
 NOVELTY - A hydrofluorination process includes reacting  
**m thylene chloride** and HF in a fluorinated polymer  
 reactor and concurrently feeding a heated recycle stream of process

reactants into the reactor.

DETAILED DESCRIPTION - A hydrofluorination process includes reacting **methylene chloride** and HF in a fluorinated polymer reactor and concurrently feeding a heated recycle stream of process reactants into the reactor.

USE - In liquid phase hydrofluorination processes for producing **difluoromethane**.

ADVANTAGE - The process eliminates corrosion in the reactor system, and exhibits efficient heat transfer and high productivity.

DESCRIPTION OF DRAWING(S) - V-1, V-2 heat exchangers

H-1, H-2 super heaters

R-1 reactor

T-1, T-2, T-3 **distillation** columns

Dwg.1/2

TECH WO 9925670 A1 UPTX: 19990802

TECHNOLOGY FOCUS - ORGANIC CHEMISTRY - Preferred Process:

The hydrofluorination process comprises:

(a) reacting **methylene chloride** and hydrogen fluoride with a catalyst, e.g. antimony pentachloride, in a fluorinated polymer reactor;

(b) **distilling** the reaction product to produce a first column bottoms product recycled to the reactor and a first column overhead product comprising hydrogen chloride, **difluoromethane**, monochloromonofluoromethane, **methylene chloride** and hydrogen fluoride;

(c) **distilling** the first column overhead in a second **distillation** column to separate hydrogen chloride as a second column overhead from a second bottoms product;

(d) **distilling** the second column bottoms product in a third **distillation** column to separate

**difluoromethane** as a third column overhead from a third column bottoms product;

(e) vaporizing and superheating the third column bottoms product; and

(f) recycling the vaporized and superheated third column bottoms product comprising monochloromonofluoromethane, **methylene chloride** and hydrogen fluoride.

The process reactants, first, second and third column bottoms recycle streams are heated to 100 - 200 degreesC and fed back to the reactor through a spurger or an eductor.

[1] 219-0-0-0 CL; 8406-0-0-0 CL PRD; 27-0-0-0 CL

KW CPI

FS AB; GI; DCN

FA CPI: A04-E10; A12-W11; E10-H03A3; N06

MC 0345-S; 0345-U; 1712-S; 1712-U

DRN UPA 20010328

PLE [1.1] 018; R00975 G0022 D01 D12 D10 D51 D53 D59 D69 D82 F- 7A; H0000; P0500 F- 7A; P0511

[1.2] 018; ND01; Q9999 Q6939-R; Q9999 Q7830; Q9999 Q8731 Q8719; K9483-R; K9676-R; K9712 K9676; Q9999 Q6973 Q6939

CMC UPB 20010328

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620

M720 M904 M905 N164 N209 N225 N309 N322 N441 N470 N513  
 DCN: R07374-K; R07374-P  
 M3 \*02\* C009 C100 C101 C730 C800 C801 C804 C805 C806 C807 M411 M730  
 M904 M905 M910  
 DCN: R01712-K; R01712-S  
 M3 \*03\* H6 H602 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M730 M904 M905 M910  
 DCN: R00345-K; R00345-S

L22 ANSWER 4 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 1998-494663 [42] WPIDS

DNC C1998-148905

TI Reduction of amount of mono chloro-mono fluoro-methane in di  
 fluoro-methane product stream - by **distillation** with  
 removal of a side-stream containing mono chloro-mono fluoro-methane,  
 useful in production of refrigerants.

DC E16 J07

IN CERRI, G; KONG, K C

PA (ALLC) ALLIED-SIGNAL INC

CYC 1

PI US 5800682 A 19980901 (199842)\* 4p B01D003-00

ADT US 5800682 A US 1996-731038 19961008

PRAI US 1996-731038 19961008

IC ICM B01D003-00

ICS C07C017-383

AB US 5800682 A UPAB: 19981021

Reduction of the amount of monochloromonofluoromethane in a product  
 stream containing **difluoromethane, dichloromethane**  
 and hydrogen fluoride comprises (a) feeding the product stream to a  
**distillation** column; (b) withdrawing a top product  
 containing **difluoromethane**; (c) obtaining a bottom product  
 containing **dichloromethane** and hydrogen fluoride; and (d)  
 withdrawing a liquid or vapour sidestream containing  
 monochloromonofluoromethane at a rate such that the amount of  
 monochloromonofluoromethane removed from the **distillation**  
 column is at least equal to the amount in the product stream.

USE - **Difluoromethane** (HFC-32) is used as a  
 replacement for environmentally disadvantageous chlorofluorocarbon  
 refrigerants. The process is useful in the production of  
 difluoromethane obtained by fluorinating **dichloromethane**  
 (HCC-30) with hydrogen fluoride over a catalyst in an isothermal or  
 adiabatic reactor.

ADVANTAGE - The process reduces the risk of personnel exposure  
 to and equipment fouling from chlorofluoromethane (HCFC-31) which is  
 a potent mutagen.

Dwg.0/0

FS CPI

FA AB; DCN

MC CPI: E10-H03A3; E10-H04B2; E11-Q01; E11-Q02; J01-A02A; J07-A08;  
 N01-C; N02; N03

DRN 0345-S; 1712-S

CMC UPB 19981021

M3 \*01\* A212 A313 A424 A425 A426 A427 A428 A429 A430 A940 C000 C009  
 C017 C100 C101 C108 C550 C730 M411 M730 M903 Q421  
 M3 \*02\* H6 H601 H602 H684 M280 M311 M321 M342 M363 M391 M416 M424  
 M620 M740 M750 M903 M904 N164 Q431 Q433 R023  
 DCN: R09219-K; R09219-X  
 M3 \*03\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424  
 M620 M720 M740 M903 M904 N164 N209 N225 N309 N322 N441 N513  
 N514 N521 N522 Q431 R023  
 DCN: R07374-K; R07374-P

L22 ANSWER 6 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 1997-529022 [49] WPIDS

DNC C1997-168426

TI Di fluoromethane production for use in refrigeration and air conditioning - by gaseous phase reaction of **methylene chloride** with hydrogen fluoride in presence of chlorine and fluorination catalyst.

DC E16 J07 X27

IN GARRAIT, D; GUIRAUD, E

PA (AQOR) ELF ATOCHEM SA; (AQOR) ATOFINA

CYC 13

PI EP 805136 A1 19971105 (199749)\* FR 9p C07C017-20

R: BE DE ES FR GB GR IT NL

FR 2748022 A1 19971031 (199751) 14p C07C019-08

AU 9719133 A 19971106 (199802) C07C017-25

JP 10053544 A 19980224 (199818) 7p C07C019-08

CA 2203434 A 19971029 (199821) C07C019-08

KR 97069960 A 19971107 (199845) C07C019-08

EP 805136 B1 20010725 (200143) FR C07C017-20

R: BE DE ES FR GB GR IT NL

DE 69705767 E 20010830 (200158) C07C017-20

ES 2160902 T3 20011116 (200201) C07C017-20

TW 448138 A 20010801 (200222) C07C017-20

ADT EP 805136 A1 EP 1997-400754 19970402; FR 2748022 A1 FR 1996-5369

19960429; AU 9719133 A AU 1997-19133 19970428; JP 10053544 A JP

1997-112623 19970430; CA 2203434 A CA 1997-2203434 19970422; KR

97069960 A KR 1997-14248 19970417; EP 805136 B1 EP 1997-400754

19970402; DE 69705767 E DE 1997-605767 19970402, EP 1997-400754

19970402; ES 2160902 T3 EP 1997-400754 19970402; TW 448138 A TW

1997-105128 19970421

FDT DE 69705767 E Based on EP 805136; ES 2160902 T3 Based on EP 805136

PRAI FR 1996-5369 19960429

REP 2.Jnl.Ref; EP 751108; JP 06263657; JP 49134612; WO 9421579; WO 9512563

IC ICM C07C017-20; C07C017-25; C07C019-08

ICS B01J027-128

ICA C07B061-00

AB EP 805136 A UPAB: 19971211

The continuous process for the preparation of

**difluoromethane** (F32) from **methylene**

**chloride** (F30) and hydrogen fluoride (HF) in the gaseous

phase and in the presence of a fluorination catalyst is claimed. The

reaction is effected in the presence of chlorine (Cl<sub>2</sub>), and the gaseous effluent from the reactor is **distilled** to separate (at the head) a flow comprising hydrogen chloride (HCl) and at least 90% of the F32, and from the base, a flow containing at least 90% of non-converted (F30, F31, and HF) reactants. F31 is chlorofluoromethane. The flow from the base is re-cycled to the reactor.

USE - Difluoromethane (F32) is a fluorinated hydrocarbon favoured as a replacement for chlorodifluoromethane (F22) and R 502 (an **azeotropic** mix of F 22 and chloropentafluoroethane) used in refrigeration and air conditioning applications. F 22 and R 502 are aggressive to the stratospheric ozone layer.

ADVANTAGE - The injection of Cl<sub>2</sub> with the reactants (F30 and HF) is more effective than oxygen (O<sub>2</sub>) in the stabilisation of catalytic activity, and also enables the direct re-cycling (without purification) of the non-reacted products (F 30, F31 and HF). The conversion rate of F 30 is close to the equilibrium state of the reaction:  $\text{CH}_2\text{Cl}_2 + 2 \text{HF} \Rightarrow \text{CH}_2\text{F}_2 + 2\text{HCl}$ , and a high selectivity (ca. 80% molar) in F 32 is attainable. Since no purification of the re-cyclate is necessary, no harmful effluents containing toxic F 31 are produced.

Dwg.1/1

FS CPI EPI

FA AB; GI; DCN

MC CPI: E10-H03A3; J07-A07; J07-A08; N03-D01

EPI: X27-F

DRN 0345-S; 1712-S; 1781-S

CMC UPB 19980119

M3 \*01\* A424 A428 C810 M411 M730 M903 Q421

M3 \*02\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620

M720 M903 M904 N209 N225 N309 N322 N441 N514 N521 N522 N523

Q433

DCN: R07374-P

L22 ANSWER 7 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 1997-202782 [18] WPIDS

DNC C1997-064914

TI Di fluoro methane prodn. from di chloro methane and hydrogen fluoride - by reacting the pre-heated starting mixt. in the presence of a fluorination catalyst and sepg. the prod. stream by **distn.**

DC A60 E16 G04 J07

IN BASS, J S; CLEMMER, P G; SMITH, A M; TUNG, H S

PA (ALLC) ALLIED-SIGNAL INC

CYC 65

PI WO 9711043 A1 19970327 (199718)\* EN 15p C07C019-08

RW: AT BE CH DE DK EA ES FI FR GB GR IE IT KE LS LU MC MW NL OA

PT SD SE SZ UG

W: AL AU BB BG BR CA CN CU CZ EE GE HU IL IS JP KP KR LK LR LT

LV MG MK MN MW MX NO NZ PL RO SD SG SI SK TR TT UA UZ VN

AU 9669775 A 19970409 (199731)

C07C019-08

US 5763708 A 19980609 (199830) C07C017-07  
 EP 854848 A1 19980729 (199834) EN C07C019-08  
 R: AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE  
 CN 1201446 A 19981209 (199917) C07C019-08  
 AU 702786 B 19990304 (199921) C07C019-08  
 HU 9901285 A2 19990728 (199936) C07C019-08  
 BR 9610669 A 19990713 (199939) C07C019-08  
 JP 11512454 W 19991026 (200002) 15p C07C017-20  
 MX 9801855 A1 19980501 (200007) C07C019-08  
 KR 99063633 A 19990726 (200043) C07C019-08  
 TW 388751 A 20000501 (200062) C07C017-20  
 US 6365580 B1 20020402 (200226) C07C019-08  
 ADT WO 9711043 A1 WO 1996-US14734 19960913; AU 9669775 A AU 1996-69775  
 19960913; US 5763708 A US 1995-530649 19950920; EP 854848 A1 EP  
 1996-930874 19960913, WO 1996-US14734 19960913; CN 1201446 A CN  
 1996-198176 19960913; AU 702786 B AU 1996-69775 19960913; HU 9901285  
 A2 WO 1996-US14734 19960913, HU 1999-1285 19960913; BR 9610669 A BR  
 1996-10669 19960913, WO 1996-US14734 19960913; JP 11512454 W WO  
 1996-US14734 19960913, JP 1997-512794 19960913; MX 9801855 A1 MX  
 1998-1855 19980309; KR 99063633 A WO 1996-US14734 19960913, KR  
 1998-702082 19980320; TW 388751 A TW 1996-111366 19960917; US  
 6365580 B1 Div ex US 1995-530649 19950920, Div ex US 1997-959748  
 19971028, US 1999-425150 19991021  
 FDT AU 9669775 A Based on WO 9711043; EP 854848 A1 Based on WO 9711043;  
 AU 702786 B Previous Publ. AU 9669775, Based on WO 9711043; HU  
 9901285 A2 Based on WO 9711043; BR 9610669 A Based on WO 9711043; JP  
 11512454 W Based on WO 9711043; KR 99063633 A Based on WO 9711043;  
 US 6365580 B1 Div ex US 5763708  
 PRAI US 1995-530649 19950920; US 1997-959748 19971028; US 1999-425150  
 19991021  
 REP 1.Jnl.Ref; EP 128510; JP 06263657; US 5208395; WO 9421579  
 IC ICM C07C017-07; C07C017-20; C07C019-08  
 ICS B01J023-26; C07C017-00; C07C017-38; C07C017-383; C07C019-00  
 ICA C07B061-00  
 AB WO 9711043 A UPAB: 19970502  
 A process for prodn. of **difluoromethane** (I) comprising the  
 steps. of (A) preheating a mixt. of HF and **dichloromethane**  
 (II) to form a vapourised and superheated compsn., (B) reacting the  
 preheated mixt. from (A) in the presence of a fluorination catalyst  
 (III) under conditions suitable to form a prod. stream comprising  
 (I), chlorofluoromethane (IV), HCl, (II) and HF; (C) recovering by  
**distn.** from the prod. stream from (B) a high boiling  
 fraction comprising HF, (II) and (IV) and a low boiling fraction  
 comprising (I), HCl, HF and reaction by-products; and (D) recovering  
 substantially pure (I) from the low boiling fraction.  
 ADVANTAGE - The process gives high prod. yield and selectivity  
 with reduced feed decomposition in comparison to prior art  
 processes.  
 Dwg.0/0  
 FS CPI  
 FA AB; DCN  
 MC CPI: A08-B04A; E10-H03A3; G04-B01; G04-B08; J07-A08; N03-D01



DRN 0345-S; 1544-S; 1712-S; 1933-S  
 PLE UPA 19970522  
 [1.1] 018; P0000; S9999 S1309-R  
 [1.2] 018; ND00  
 [1.3] 018; G2686-R D00 F20 Cr 6B Tr O- 6A; C999 C102 C000; C999 C260  
 [1.4] 018; D01 D11 D10 D50 D69 D81 F- 7A; A999 A282 A260; A999 A759; L9999 L2255 L2222; L9999 L2120; N9999 N6177-R; N9999 N6213 N6177; N9999 N6735-R N6655; N9999 N6928; B9999 B4535

CMC UPB 19970619  
 M3 \*01\* A313 A424 A940 C108 C550 C730 M411 M730 M903 Q421  
 M3 \*02\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M720 M903 M904 N209 N225 N309 N322 N421 N441 N480 N513 N514  
 Q120 Q337  
 DCN: R07374-P

L22 ANSWER 8 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1997-089032 [09] WPIDS

DNC C1997-029010

TI Di fluoromethane prodn. - by catalytic gas phase fluorination of **methylene chloride** with anhydrous hydrogen fluoride in presence of chlorine.

DC E16 J04

IN CHEMINAL, B; LACROIX, E; LANTZ, A; PERDRIEUX, S; REQUIEME, B; LAMTZ, A

PA (AQOR) ELF ATOCHEM SA

CYC 15

PI EP 751108 A1 19970102 (199709)\* FR 8p C07C017-20

R: BE DE ES FR GB GR IT NL  
 AU 9656272 A 19970109 (199710) C07C019-08  
 FR 2736050 A1 19970103 (199711) 11p C07C019-08  
 JP 09020696 A 19970121 (199713) 7p C07C019-08  
 CA 2180283 A 19961230 (199718) FR C07C019-08  
 KR 97001290 A 19970124 (199803) C07C019-08  
 TW 324004 A 19980101 (199827) C07C019-08  
 AU 700839 B 19990114 (199914) C07C019-08  
 EP 751108 B1 20000112 (200008) FR C07C017-20  
 R: BE DE ES FR GB GR IT NL  
 DE 69606102 E 20000217 (200016) C07C017-20  
 ES 2142553 T3 20000416 (200026) C07C017-20  
 CN 1144213 A 19970305 (200064) C07C019-08  
 US 6242659 B1 20010605 (200133) C07C017-08  
 US 2001003786 A1 20010614 (200135) C07C021-18

ADT EP 751108 A1 EP 1996-401151 19960529; AU 9656272 A AU 1996-56272 19960701; FR 2736050 A1 FR 1995-7821 19950629; JP 09020696 A JP 1996-167732 19960627; CA 2180283 A CA 1996-2180283 19960628; KR 97001290 A KR 1996-25898 19960629; TW 324004 A TW 1996-107123 19960613; AU 700839 B AU 1996-56272 19960701; EP 751108 B1 EP 1996-401151 19960529; DE 69606102 E DE 1996-606102 19960529, EP 1996-401151 19960529; ES 2142553 T3 EP 1996-401151 19960529; CN 1144213 A CN 1996-108649 19960626; US 6242659 B1 US 1996-663634 19960614; US 2001003786 A1 Cont of US 1996-663634 19960614, US

2001-761845 20010118  
 FDT AU 700839 B Previous Publ. AU 9656272; DE 69606102 E Based on EP 751108; ES 2142553 T3 Based on EP 751108  
 PRAI FR 1995-7821 19950629  
 REP 1.Jnl.Ref; JP 49134612; US 3183276; US 38551512; WO 9421580  
 IC ICM C07C017-08; C07C017-20; C07C019-08; C07C021-18  
 ICS B01J027-132; C07C017-35  
 ICA C07B061-00  
 AB EP 751108 A UPAB: 19970228  
**Difluoromethane** (I) is prepd. by catalytic gas phase fluorination of **methylene chloride** (II) with anhydrous HF in the presence of chlorine.  
 USE - (I) (F32) is a useful replacement for F22(chlorodifluoromethane) and F502 (**azeotropic** mixt. of F22 and chloropentafluoroethane) in fluorohydrocarbon mixts. for use in refrigeration and air conditioning units.  
 ADVANTAGE - (I) does not affect the ozone layer and is thus environmentally safer than CFCs previously used in refrigerant mixes. The process gives high conversions and good selectivity to the prodn. of (I) whilst maintaining good catalyst stability and freedom from coking.  
 Dwg.0/0  
 CPI  
 FS AB; DCN  
 MC CPI: E10-H03A3; J04-E01; N03-D01  
 DRN 0345-S; 1712-S; 1726-S; 1781-S; 1926-S; 1933-S  
 CMC UPB 19970424  
 M3 \*01\* A423 A424 A428 A940 C017 C100 C108 C550 C730 M411 M730 M903 Q421  
 M3 \*02\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620 M720 M903 M904 N209 N225 N309 N322 N426 N441 N513 N514 N522 Q433  
 DCN: R07374-P  
 L22 ANSWER 9 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1997-089031 [09] WPIDS  
 DNN N1997-073250 DNC C1997-029009  
 TI Di fluoromethane prodn. - by catalytic gas phase fluorination of **methylene chloride** with anhydrous hydrofluoric acid using chromium catalyst.  
 DC E16 J04 X27  
 IN LACROIX, E; LANTZ, A; REQUIEME, B; LAMTZ, A  
 PA (AQOR) ELF ATOCHEM SA  
 CYC 15  
 PI EP 751107 A1 19970102 (199709)\* FR 8p C07C017-20  
 R: BE DE ES FR GB GR IT NL  
 AU 9656290 A 19970109 (199710) C07C019-08  
 FR 2736048 A1 19970103 (199711) 13p C07C019-08  
 JP 09012488 A 19970114 (199712) 7p C07C019-08  
 CA 2179536 A 19961228 (199717) FR C07C019-08  
 KR 97001289 A 19970124 (199803) C07C019-08  
 TW 328071 A 19980311 (199832) C07C019-08

US 5900514 A 19990504 (199925) C07C019-08  
 AU 714842 B 20000113 (200014) C07C019-08  
 CN 1150943 A 19970604 (200131) C07C019-08  
 ADT EP 751107 A1 EP 1996-401150 19960529; AU 9656290 A AU 1996-56290  
 19960627; FR 2736048 A1 FR 1995-7705 19950627; JP 09012488 A JP  
 1996-167734 19960627; CA 2179536 A CA 1996-2179536 19960619; KR  
 97001289 A KR 1996-24202 19960626; TW 328071 A TW 1996-107120  
 19960613; US 5900514 A US 1996-663977 19960614; AU 714842 B AU  
 1996-56290 19960627; CN 1150943 A CN 1996-108650 19960626  
 FDT AU 714842 B Previous Publ. AU 9656290  
 PRAI FR 1995-7705 19950627  
 REP 1.Jnl.Ref; EP 328127; EP 554165; JP 51082206; US 2745886  
 IC ICM C07C017-20; C07C019-08  
 ICS B01J023-86; C07C017-158; C07C017-35  
 ICA C07B061-00  
 AB EP 751107 A UPAB: 19970228  
 Difluoromethane (I) is prepd. by catalytic gas phase  
 fluorination of **methylene chloride** (II) with  
 anhydrous HF in the presence of 0.1-5 moles of O2 per 100 moles of  
**methylene chloride** (II) at 330-450deg.C and in the  
 presence of a solid or supported Cr catalyst.  
 USE - (I) (F32) is a useful replacement for F22  
 (chlorodifluoromethane) and F502 (an **azeotropic** mixt. of  
 F22 and chloropentafluoroethane) in fluorohydrocarbon mixts. for use  
 in refrigeration and air conditioning units.  
 ADVANTAGE - (I) does not affect the ozone layer and is thus  
 environmentally safer than CFCs previously used in refrigerant  
 mixes. The process gives high conversions and good selectivity to  
 the prodn. of (I) whilst maintaining good catalyst stability and  
 freedom from coking.  
 Dwg.0/0  
 FS CPI EPI  
 FA AB; DCN  
 MC CPI: E10-H03A3; J04-E01; N03-D01  
 EPI: X27-F  
 DRN 0345-S; 1712-S; 1779-S; 1933-S  
 CMC UPB 19970424  
 M3 \*01\* A424 A940 C009 C100 C108 C550 C730 C810 M411 M730 M903 Q421  
 M3 \*02\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M720 M903 M904 N209 N225 N309 N322 N411 N426 N441 N514 N522  
 Q433  
 DCN: R07374-P  
 L22 ANSWER 10 OF 15 WPIDS (C) 2002 THOMSON DERWENT  
 AN 1996-139086 [14] WPIDS  
 DNN N1996-116531 DNC C1996-043702  
 TI Prodn. of di fluoro-methane useful as refrigerant - by liq. phase  
 reaction of **methylene chloride** with hydrogen  
 fluoride in the presence of an antimony penta chloride catalyst.  
 DC E16 J07 X27  
 IN KIM, D S; NA, DOO C; NAM, K H; NA, D C  
 PA (ULSA-N) ULSAN CHEM CO LTD; (UTSU-N) UTSUYAMA KAGAKU KK

CYC. 3

PI US 5495057 A 19960227 (199614)\* 6p C07C017-08  
 FR 2728895 A1 19960705 (199634) 15p C07C019-08  
 JP 08183748 A 19960716 (199638) 6p C07C019-08  
 JP 2840929 B2 19981224 (199905) 6p C07C019-08  
 ADT US 5495057 A US 1995-398965 19950302; FR 2728895 A1 FR 1995-4044  
 19950405; JP 08183748 A JP 1995-59050 19950317; JP 2840929 B2 JP  
 1995-59050 19950317

FDT JP 2840929 B2 Previous Publ. JP 08183748

PRAI KR 1994-38154 19941228

IC ICM C07C017-08; C07C019-08

ICS B01J027-10; C07C017-20

ICA C07B061-00

AB US 5495057 A UPAB: 19960405

Prepn. of difluoromethane (CH<sub>2</sub>F<sub>2</sub>) comprises liq.

phase reaction of methylene chloride (

CH<sub>2</sub>Cl<sub>2</sub>) with hydrogen fluoride at 70-90deg.C in the presence  
 of an antimony penta-chloride (SbCl<sub>5</sub>) catalyst, using a mole ratio  
 of catalyst to CH<sub>2</sub>Cl<sub>2</sub> to 0.05-0.17.

The concn. of pentavalent antimony (Sb<sup>5+</sup>) is maintained at 85%,  
 and the reaction is carried out at a pressure of 11-12 kg/cm<sup>2</sup>.g.

In an example, 1100 kg CH<sub>2</sub>Cl<sub>2</sub> and 59.85 kg SbCl<sub>5</sub> were  
 reacted with HF at mole ratios of HF/CH<sub>2</sub>Cl<sub>2</sub> of 2.0/1. The  
 reaction was at 90deg.C and at 11-12 kg/cm<sup>2</sup>.g, giving a selectivity  
 to CH<sub>2</sub>F<sub>2</sub> of 93.52% at 93.6% CH<sub>2</sub>Cl<sub>2</sub> conversion.

USE - Difluoromethane is useful as a  
 zero-ozone-depletion potential replacement for chlorodifluoromethane  
 in (azeotropic) refrigerant compsns..

ADVANTAGE - The reaction is applicable on an industrial scale,  
 giving high conversions (93.6%) and selectivities (e.g. 93.5%),  
 compared to, e.g., US Patents 2649374 and 2749375 (e.g. 83-89%  
 conversion). The catalyst gives higher reaction rates than prior  
 SbF<sub>3</sub> catalysts; is liq., providing a semi-permanent life-span; and  
 is cheap and easy to purchase.

Dwg.0/1

FS

FA AB; DCN

MC CPI: E10-H03A3; J07-A08; N03-H; N04-D01

EPI: X27-F

DRN 0345-S; 1712-S

CMC UPB 19960705

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M720 M903 M904 N209 N225 N309 N322 N441 N513 Q433 R023  
 DCN: R07374-P

M3 \*02\* A351 A940 C017 C100 C730 M411 M730 M903 Q421

L22 ANSWER 11 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 1995-294297 [39] WPIDS

DNC C1995-132387

TI Sepn. of hydrogen fluoride and di fluoromethane - by distn  
 . and/or fractional condensn..

DC E16 J07

IN GALLAND, J; ROUZIES, D

PA (AQOR) ELF ATOCHEM SA

CYC 13

PI EP 669303 A1 19950830 (199539)\* FR 13p C07C017-38

R: BE DE ES FR GB GR IT NL

AU 9512253 A 19950907 (199544) C07C017-383

CA 2143268 A 19950829 (199548) FR C01B007-19

JP 07258125 A 19951009 (199549) 8p C07C019-08

CN 1112540 A 19951129 (199738) C07C017-38

EP 669303 B1 19971029 (199748) FR 14p C07C017-38

R: BE DE ES FR GB GR IT NL

DE 69500938 E 19971204 (199803) C07C017-38

US 5707497 A 19980113 (199809) 8p B01D003-36

ES 2110293 T3 19980201 (199811) C07C017-38

AU 697339 B 19981001 (199851) C07C017-383

JP 3279449 B2 20020430 (200230) 8p C07C017-383

ADT EP 669303 A1 EP 1995-400126 19950123; AU 9512253 A AU 1995-12253 19950214; CA 2143268 A CA 1995-2143268 19950223; JP 07258125 A JP 1995-39910 19950228; CN 1112540 A CN 1995-100859 19950228; EP 669303 B1 EP 1995-400126 19950123; DE 69500938 E DE 1995-600938 19950123, EP 1995-400126 19950123; US 5707497 A US 1995-394983 19950227; ES 2110293 T3 EP 1995-400126 19950123; AU 697339 B AU 1995-12253 19950214; JP 3279449 B2 JP 1995-39910 19950228

FDT DE 69500938 E Based on EP 669303; ES 2110293 T3 Based on EP 669303; AU 697339 B Previous Publ. AU 9512253; JP 3279449 B2 Previous Publ. JP 07258125

PRAI FR 1994-2231 19940228

REP WO 9321140

IC ICM B01D003-36; C01B007-19; C07C017-38; C07C019-08

ICS B01D003-36; C01B007-19; C07C019-08

AB EP 669303 A UPAB: 19951004

A process for the sepn. of HF and F.32 by **distn.** and/or fractional condensn. in one or more stages is claimed. Process comprises at least one stage to give a flow of HF and F.32 content corresp. to those of the **azeotropic** mixt. which is effected at a pressure such that the partial pressure of the (HF+F32) mixt. (Pa expressed in bars abs.) and the HF content (xwt.%) meet the equation:  $Pa = 17-22.9(x+0.821)\ln(x+0.608)+56.6[\ln(x+0.608)]^2$

USE - The process is used essentially to separate non-transformed HF contained in mixts. resulting from the mfr. of F.32 by fluorination of **methylene chloride**, for recycling in anhydrous form to the fluorination reactor, and to recover F.32 significantly free of HF and thus facilitate its final purificn. F.32 is a substitute for CFC's.

ADVANTAGE - Techniques used in the sepn. of HF from chlorofluorinated or fluorinated cpds. (which readily form **azeotropes**) are either uneconomic or inapplicable to the sepn. of HF from F.32. It has now been found that the HF-F.32 **azeotrope** behaves uniquely in that the content of HF drops considerably with increase of pressure and becomes very low (less than 3000 ppm wt.) about 20 bar absolute. The property enables

efficient industrial sepn. of HF and F.32, partic. the recovery of non-transformed HF in mixts. from mfr. of F.32 by fluorination of **methylene chloride** with HF and/or to obtain F.32 practically free from HF. The process can also be applied to the sepn. of crude mixts. resulting from processes either of the liq. phase type (usually catalysed by antimony chlorofluorides) or vapour phase reactions using heterogeneous catalysts such as Cr. The mixts. may thus contain HCl, Cl<sub>2</sub>, chlorofluoromethanes (F.31, F.27) and trifluoromethane (F.23).

Dwg.0/4

ABEQ EP 669303 B UPAB: 19971209

Process for the separation of hydrogen fluoride (HF) and of **difluoromethane** (F32) by fractional **distillation** and/or condensation, in one or more stages, characterized in that it includes at least one stage making it possible to obtain a stream whose HF and F32 contents correspond substantially to those of the **azeotropic** composition, the said stage being performed, as a function of the intended separation objective, at a pressure chosen so that the partial pressure of the HF + F32 mixture of the said stream (Pa expressed in bars absolute) and the HF content of the said mixture (x in per cent by weight) are linked by the relationship;  $P_a = 17-22.9(x+0.821)\ln(x+0.608)+56.6(\ln(x+0.608))^2$

Dwg.0/4

ABEQ US 5707497 A UPAB: 19980302

A process for the sepn. of HF and F.32 by **distn.** and/or fractional condensn. in one or more stages is claimed. Process comprises at least one stage to give a flow of HF and F.32 content corresp. to those of the **azeotropic** mixt. which is effected at a pressure such that the partial pressure of the (HF+F32) mixt. (Pa expressed in bars abs.) and the HF content (xwt.%) meet the equation:  $P_a = 17-22.9(x+0.821)\ln(x+0.608)+56.6[\ln(x+0.608)]^2$

USE - The process is used essentially to separate non-transformed HF contained in mixts. resulting from the mfr. of F.32 by fluorination of **methylene chloride**, for recycling in anhydrous form to the fluorination reactor, and to recover F.32 significantly free of HF and thus facilitate its final purificn. F.32 is a substitute for CFC's.

ADVANTAGE - Techniques used in the sepn. of HF from chlorofluorinated or fluorinated cpds. (which readily form **azeotropes**) are either uneconomic or inapplicable to the sepn. of HF from F.32. It has now been found that the HF-F.32 **azeotrope** behaves uniquely in that the content of HF drops considerably with increase of pressure and becomes very low (less than 3000 ppm wt.) about 20 bar absolute. The property enables efficient industrial sepn. of HF and F.32, partic. the recovery of non-transformed HF in mixts. from mfr. of F.32 by fluorination of **methylene chloride** with HF and/or to obtain F.32 practically free from HF. The process can also be applied to the sepn. of crude mixts. resulting from processes either of the liq. phase type (usually catalysed by antimony chlorofluorides) or vapour phase reactions using heterogeneous catalysts such as Cr. The mixts.

may thus contain HCl, Cl<sub>2</sub>, chlorofluoromethanes (F.31, F.27) and trifluoromethane (F.23).

Dwg.0/4

FS

CPI

FA

AB; DCN

MC

CPI: E10-H03A3; E11-Q01; E31-B03C; J01-A02A; J07-D02

DRN

0345-S; 1712-P; 1712-U

CMC

UPB 19951215

M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M424

M620 M720 M903 M904 N164 N522 Q431

DCN: R07374-P

M3 \*02\* C009 C100 C101 C730 C800 C801 C804 C805 C806 C807 M411 M424

M720 M750 M903 M904 M910 N164 N522 Q431

DCN: R01712-P; R01712-X

M3 \*03\* A351 A424 C810 M411 M730 M903 Q421

L22 ANSWER 12 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN

1995-185708 [24] WPIDS

DNC

C1995-086280

TI

Di fluoromethane prodn., useful as chloro-fluoro-carbon replacement  
- by gas phase contact of di chloromethane and hydrogen fluoride  
over a carbon supported trivalent chromium catalyst, used as  
refrigerant.

DC

E16 J04

IN

FURMANEK, P S; GLASSCOCK, D A; KEANE, M; MAHLER, B A; RAO, V; RAO, V  
N M

PA

(DUPO) DU PONT DE NEMOURS & CO E I

CYC

18

PI

WO 9512563 A1 19950511 (199524)\* EN 27p C07C017-20

RW: AT BE CH DE DK ES FR GB GR IE IT LU MC NL PT SE

W: JP

EP 726887 A1 19960821 (199638) EN C07C017-20

R: DE ES FR GB IT NL

JP 09504552 W 19970506 (199728) 25p C07C019-08

EP 726887 B1 19981014 (199845) EN C07C017-20

R: DE ES FR GB IT NL

DE 69413995 E 19981119 (199901) C07C017-20

ES 2124434 T3 19990201 (199911) C07C017-20

US 5955637 A 19990921 (199945) C07C019-08

US 6274781 B1 20010814 (200148) C07C017-08

ADT WO 9512563 A1 WO 1994-US12473 19941031; EP 726887 A1 EP 1994-932126

19941031, WO 1994-US12473 19941031; JP 09504552 W WO 1994-US12473

19941031, JP 1995-513331 19941031; EP 726887 B1 EP 1994-932126

19941031, WO 1994-US12473 19941031; DE 69413995 E DE 1994-613995

19941031, EP 1994-932126 19941031, WO 1994-US12473 19941031; ES

2124434 T3 EP 1994-932126 19941031; US 5955637 A Div ex US

1993-146334 19931101, US 1995-458604 19950602; US 6274781 B1 US

1993-146334 19931101

FDT EP 726887 A1 Based on WO 9512563; JP 09504552 W Based on WO 9512563;

EP 726887 B1 Based on WO 9512563; DE 69413995 E Based on EP 726887,

Based on WO 9512563; ES 2124434 T3 Based on EP 726887

PRAI US 1993-146334 19931101; US 1995-458604 19950602

REP 4.Jnl.Ref; EP 403108; JP 59225131; JP 60013726  
 IC ICM C07C017-08; C07C017-20; C07C019-08  
 ICS C07C017-35; C07C019-10; C07C019-12; C07C021-00  
 ICA B01J027-12; C07B061-00  
 AB WO 9512563 A UPAB: 19950626

**Difluoromethane** (HFC-22) prodn., comprises gas phase contact of **dichloromethane** and HF over a C-supported Cr(III) catalyst having an ash content of less than 0.5 wt.%, at 180-375 deg.C. Also claimed are **azeotropic** or **azeotrope**-like compsns.

USE - **Difluoromethane** is a proposed replacement for chlorofluorocarbons (CFCs) which may be detrimental to the Earth's ozone layer and which have been used in refrigeration and air-conditioning.

ADVANTAGE - The catalyst and temp. conditions allow concurrent reaction of 1,1,1-trichlorotrifluoroethane (CCl3CF3, CFC-113a) with HF to form 1,1-dichlorotetrafluoroethane (CCl2F2CF3, CFC-114a), which is an intermediate of interest for prodn. of 1,1,1,1-tetrafluoroethane (CF3CH2F, HFC-134a), which in turn is an environmentally acceptable replacement for CFC refrigerants, blowing agents, aerosol propellants and sterilants.

Dwg.0/0

FS CPI  
 FA AB; DCN  
 MC CPI: E10-H03A3; J04-E01; J07-A08; N03-D01  
 DRN 0345-S; 1712-S  
 CMC UPB 19950905  
 M3 \*01\* H6 H601 H608 H684 M280 M311 M321 M342 M363 M391 M416 M620  
 M720 M903 M904 N209 N225 N309 N322 N441 N514 Q337 Q433  
 DCN: R07374-P  
 M3 \*02\* A424 A940 C017 C100 C730 M411 M730 M903 Q421

L22 ANSWER 14 OF 15 WPIDS (C) 2002 THOMSON DERWENT

AN 1993-351586 [44] WPIDS

DNC C1993-156015

TI **Azeotropic** mixt. of hydrogen fluoride and di chloromethane, di fluoromethane or chloro-fluoromethane - used to remove hydrogen fluoride simply, without causing pollution.

DC E16

IN KOMATSU, S; KOYAMA, S; MATSUMOTO, T; TANAKA, Y; TSUDA, T

PA (DAIK) DAIKIN IND LTD; (DAIK) DAIKIN KOGYO KK

CYC 25

PI WO 9321140 A1 19931028 (199344)\* JA 31p C07C019-02  
 W: AT AU BE BR CA CH DE DK ES FR GB GR IE IT JP KR LU MC NL PT  
 RU SE US  
 AU 9339040 A 19931118 (199410) C07C019-02  
 JP 05518174 X 19940407 (199419) C07C019-02  
 EP 606482 A1 19940720 (199428) EN 16p C07C019-02  
 R: BE DE ES FR GB IT NL  
 BR 9305484 A 19950411 (199521) C07C019-01  
 CN 1088195 A 19940622 (199531) C07C017-38  
 AU 663586 B 19951012 (199548) C07C019-02



US 5523015 A 19960604 (199628) 10p C07C017-38  
 TW 283659 A 19960821 (199702) B01D005-00  
 EP 606482 B1 19980715 (199832) EN C07C019-00  
 R: BE DE ES FR GB IT NL  
 DE 69319711 E 19980820 (199839) C07C019-00  
 ES 2118949 T3 19981001 (199848) C07C019-00  
 RU 2118635 C1 19980910 (200007) C07C017-38  
 JP 3147380 B2 20010319 (200125) 11p C07C019-03  
 JP 2001174147 A 20010629 (200141) 10p F25J001-00  
 US 6311515 B1 20011106 (200170) F25J003-00  
 KR 295306 B 20010917 (200231) C07C019-02  
 ADT WO 9321140 A1 WO 1993-JP455 19930409; AU 9339040 A AU 1993-39040  
 19930409; JP 05518174 X JP 1993-518174 19930409, WO 1993-JP455  
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 1993-162010 19931209; TW 283659 A TW 1993-102792 19930413; EP 606482  
 B1 EP 1993-908071 19930409, WO 1993-JP455 19930409; DE 69319711 E DE  
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 JP 2000-316594 19930409; US 6311515 B1 Div ex US 1997-967539  
 19971112, US 2000-593523 20000614; KR 295306 B WO 1993-JP455  
 19930409, KR 1993-703863 19931213  
 FDT AU 9339040 A Based on WO 9321140; JP 05518174 X Based on WO 9321140;  
 EP 606482 A1 Based on WO 9321140; BR 9305484 A Based on WO 9321140;  
 AU 663586 B Previous Publ. AU 9339040, Based on WO 9321140; US  
 5523015 A Based on WO 9321140; EP 606482 B1 Based on WO 9321140; DE  
 69319711 E Based on EP 606482, Based on WO 9321140; ES 2118949 T3  
 Based on EP 606482; JP 3147380 B2 Based on WO 9321140; KR 295306 B  
 Previous Publ. KR 94701373  
 PRAI JP 1992-92667 19920413; JP 1992-107656 19920427  
 REP JP 02167803; JP 02295937; JP 02295938; US 4911792; US 4950364; US  
 4975156  
 IC ICM B01D005-00; C07C017-38; C07C019-00; C07C019-01; C07C019-02;  
 C07C019-03; F25J001-00; F25J003-00  
 ICS B01D003-36; C01B007-19; C07C017-383; C07C019-08; C07C019-10  
 AB WO 9321140 A UPAB: 19940524  
 HF can be efficiently removed from a mixture of HF with  
 CCl<sub>2</sub>H<sub>2</sub>. CCl<sub>2</sub>H<sub>2</sub> and/or CF<sub>2</sub>H<sub>2</sub>, by distilling  
 the mixture so as to remove HF as a binary azeotropic  
 mixture.

When the mole ratio of CCl<sub>2</sub>H<sub>2</sub> to HF is less than 4, CCl<sub>2</sub>H<sub>2</sub> is  
 added to the mixture so as to produce the mole ratio of 4 or more  
 and then the mixture is distilled so as to remove HF as a  
 binary azeotropic mixture, HF(CF<sub>2</sub>H<sub>2</sub>), HF(CCl<sub>2</sub>H<sub>2</sub>)  
 and/or CCl<sub>2</sub>H<sub>2</sub>). The pressure during distillation  
 of the mixture is pref. 0.5-30 kg/cm<sup>2</sup>.

A mixture contg. at least HF and CCl<sub>2</sub>H<sub>2</sub> is cooled to -20 deg.C  
 or lower so as to separate it into two phases, an upper liq. phase

rich in HF and a lower liq. phase poor in HF. The  $\text{CCl}_2\text{FH}_2$  contg. less HF is collected. A mixture contg. at least HF,  $\text{CCl}_2\text{FH}_2$  and  $\text{CCl}_2\text{H}_2$  is enriched with  $\text{CCl}_2\text{H}_2$  so as to produce a mole ratio of  $\text{CCl}_2\text{H}_2/\text{CCl}_2\text{FH}_2$  of 0.5 or more.

USE/ADVANTAGE - This method can remove HF efficiently from the mixture without using a large amount of alkaline cpd. Since in this method the **azeotropic** temps. used are 12 deg.C, -11 deg.C and -53 deg.C, the method and apparatus system can be simple. The method does not contaminate the environment.

Dwg. 0/2

ABEQ US 5523015 A UPAB: 19960719

An **azeotropic** mixture consists of **dichloromethane** and hydrogen fluoride.

Dwg.0/2

FS CPI

FA AB; DCN

MC CPI: E10-H02B; E10-H02D; E11-Q01; E11-Q02; E31-B02

DRN 0345-P; 1712-U

CMC UPB 19940217

M3 \*01\* C009 C100 C101 C730 C800 C801 C804 C805 C806 C807 M411 M424  
M750 M903 M904 M910 N164 N511 N512 Q431

DCN: R01712-X

M3 \*02\* H6 H601 H602 H608 H684 M280 M311 M321 M342 M363 M391 M416  
M424 M620 M720 M903 M904 N164 N511 N512 Q431

DCN: R00345-P; R07374-P; R09219-P